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The Effect of Addition of Fluorescent Moieties to Dihydropyrenes: Enhancing Photochromicity and Fluorescence Monitoring

Reginald H. Mitchell,* Cornelia Bohne,* Stephen G. Robinson, and Yanhong Yang

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, Canada V8W 3V6

regmitch@uvic.ca

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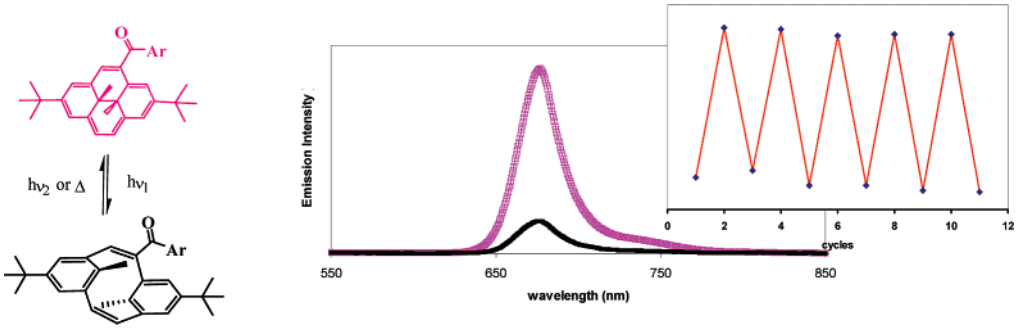
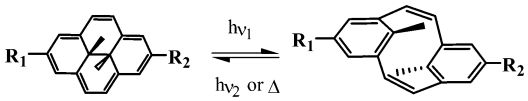


A series of dihydropyrenes with appending fluorescent moieties were synthesized with the objective of increasing the photochromic efficiency for this class of compounds and to establish how suitable fluorescence would be to follow their photochromic behavior. The ring opening quantum yields of dihydropyrenes with aroyl substituents at the 4-position showed increased ring opening quantum yields without a decrease of the half-life for the thermal reversion of the less stable open isomer, the metacyclophanediene to the dihydropyrene. The fluorescence of the appending naphthoyl or pyrenoyl moieties was not suitable to follow the photochromic cycling of the dihydropyrenes. However, the emission detected above 600 nm of the closed isomer of the dihydropyrene moiety was shown to be a good monitoring method for the photochromic cycling.

Introduction

Dihydropyrenes (DHPs) such as **1** belong to the diarylethene class of photochromes. Because the colorless open form (the cyclophanediene, CPD), **1-o**, reverts both photochemically and thermally to the colored more stable closed form, **1-c**, they are called negative-T-photochromes.[1] Such systems are less well-known and studied than



1-c	$R_1, R_2 = H$	**1-o**
2-c	$R_1, R_2 =$ t-Bu	**2-o**
3-c	$R_1 =$ CHO, $R_2 = H$	**3-o**

the more popular positive-photochromes,[2] where the thermodynamically stable form is the colorless isomer. The green parent, **1-c**, is actually not a very good photochrome because the quantum yield of ring opening with visible light to yield **1-o** is only 0.006.[3] Moreover, the quantum yield for ring opening of the synthetically more accessible[4−6] di-*tert*-butyl derivative, **2-c**, is four times less, 0.0015[3] (0.0018).[7] Even in 1970,[8] it was known that introduction of a formyl group at the 2-position of **1** to give **3-c** considerably enhanced (∼10 times) the photochemical conversion to **3-o**. Unfortunately, the thermal return rate was also increased, ∼50 times, such that at room temperatures the photochromism of **3** was less useful. One objective

* To whom correspondence should be addressed. Phone: 250-721-7159. Fax: 250-721-7147. Address synthetic correspondence to regmitch@uvic.ca, and address photochemistry correspondence to bohne@uvic.ca.

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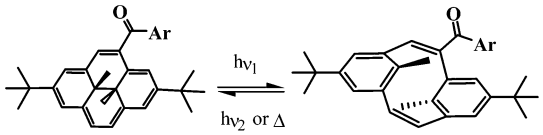
of this paper was to find derivatives of **2** which had improved ring opening quantum yields and reasonably slow thermal return reactions since, frequently, an increase in the ring opening quantum yield led to a decrease in the thermal stability of the open isomer. A second objective was to investigate the use of fluorescence to monitor the photochromic cycling, namely, the state of the ring opening/closing reactions. Introduction of fluorescence moieties is attractive because of the sensitivity of fluorescence when compared to absorption measurements. A further advantage of using fluorescence in the case of DHP derivatives is that, as will be shown, the photochromic cycling can be monitored at wavelengths where interference from multiple absorptions is absent.

Aroyl substituents seemed attractive because they lack the easy oxidation of a formyl group and, based on previous reports, looked promising: in 1967, Boekelheide[9] reported the syntheses of 2-benzoyl-**1-c**, and in 1970, Blattmann[8] reported that this compound had a photo-opening quantum yield similar to that of the formyl compound **3-c**. Similarly, Tashiro[7] in 1988 reported quantum yields and kinetic data for a series of derivatives of **2-c**, including 4-benzoyl-**2-c** (=**4-c** below), but without any synthetic details (then or since). The data for the latter, however, indicated that the photo-opening quantum yield was about 2.6 times higher than that of its parent **2-c**, while the thermal closing was 1.5 times faster.

Fluorescence has been used for different photochromic systems,[10a−c] where the photochromic moiety itself provides the fluorescent chromophore or a chromophore is appended to the photochromic framework. The advantage of using a pendant fluorescent moiety is that excitation of this reporter moiety may not lead to switching of the photochrome when the fluorescent and photochromic moieties are isolated, that is, no energy transfer occurs. These two moieties can be isolated by using nonconjugating spacers, such as, for example, the short bicyclo-[1.1.1]pentane.[10d] Modulation of the fluorescence intensity and spectra of a particular photochrome can be achieved by changing the extent of conjugation or by changes in the efficiency of energy or electron transfer between the various chromophores in the molecule for each of the isomers.[10b,c] An additional advantage of fluorescence is the ability to detect the emission from single molecules. For example, the intramolecular quenching by the closed isomer of a diarylethene of a fluorescent moiety was employed to follow the photocycling by single molecule detection.[10e,f] The ability of using fluorescence to follow the photochromism of dihydropyrenes has not been explored to date, despite the fact that **2-c** was shown to be weakly fluorescent ($\phi = 0.002$) with a very structured emission spectrum above 600 nm.[3] In the case of [*e*]-annelated dihydropyrenes, both the closed and open isomers show weak fluorescence,[11] where the closed isomer emits above 600 nm and the open isomer shows, in some cases, an emission at shorter wavelengths similar to that of the annelated polyaromatic hydrocarbons. In this work, we combined the use of a carbonyl spacer with aromatic moieties (**4**−**7**) of which naphthalene, anthracene, and pyrene are known to be fluorophores with high fluorescence quantum yields. The thermal ring closing rate constants for the synthesized compounds were initially studied, and for the promising candidates, photophysical experiments were performed.



4-c	**Ar = Phenyl**	**4-o**
5-c	**Ar = 1-Naphthyl**	**5-o**
6-c	**Ar = 9-Anthracenyl**	**6-o**
7-c	**Ar = 1-Pyrenyl**	**7-o**

Results and Discussion

Syntheses: Dihydropyrenes are sensitive to Lewis acid conditions, and sometimes rearranged products, where the internal groups have migrated, are obtained.[12,13] With care, however, reaction of the di-*tert*-butyl parent **2-c** with the appropriate acid chloride and $AlCl_3$ in CH_2Cl_2 at 20 °C for 2−6 h gave the products **4-c**−**7-c** as greenish-brown solids in 50−97% yields. Full characterization for each compound is given in the Experimental Section. In each case, new ^{1}H NMR peaks for the internal methyl protons were observed around δ −4, which is characteristic of dihydropyrenes, in which the internal protons are very shielded by the strong diatropic ring current. Specifically, the peaks appear slightly deshielded from those of the parent **2-c** (δ −4.06) and no longer identical to each other, and for **4-c**, they are at δ −3.83, −3.84; for **5-c**, at δ −3.81, −3.84; for **6-c**, at δ −3.81, −3.86; and for **7-c**, at δ −3.75, −3.78. Also, new IR C=O stretching bands at 1630−1640 cm^{-1} were observed. Interestingly, the anthranoyl compound **6-c** showed restricted rotation, resulting in broad peaks for H-3,5,6 and the 2-*t*-Bu group protons of the dihydropyrenes at ambient temperatures. All of these peaks sharpen on cooling to 210 K or on heating to 380 K. In addition, the anthracenyl protons, H-1′,8′, are a doublet at δ 7.98 at 325 K, where rotation is fast on the NMR time scale, but collapse in to a broad singlet at 280 K (=T_c) and re-emerge as two doublets at 210 K, where rotation is slow. The separation, $\Delta\nu = 36.3$ Hz, suggests[14] a $\Delta G_c^{\ddagger}$ of 14 kcal/mol for the rotational process.

While the purity of **4-c**−**7-c** was suitable for basic photochemical opening/closing and thermal closing studies, for detailed photophysical measurements, very high purity compounds were required. Compounds **5-c** and **7-c** were suitably pure (≥99.5%) by HPLC (see Experimental Section) to conduct these latter experiments. The fluorescent impurities in **4-c** and **6-c** and their instability during extensive irradiation precluded quantitative photophysical experiments, such as quantum yield determination. Also, for comparison purposes, four additional

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(14) See: Dixon, K. R.; Mitchell, R. H. *Can. J. Chem.* **1983**, *61*, 1598−1602 and the references therein.

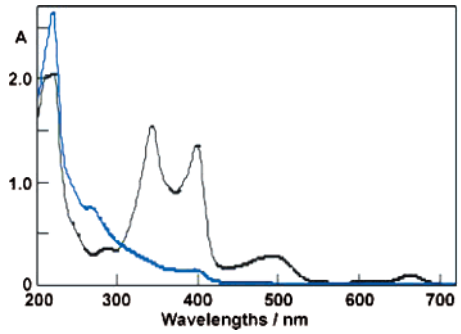
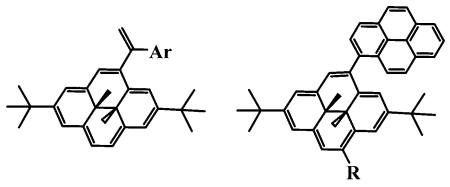


FIGURE 1. Absorption spectra of the DHP isomer **7-c** in cyclohexane (black) and of the solution after 30 min irradiation above 500 nm (blue, mainly the CPD isomer **7-o**).

compounds **8**−**11** were prepared with similar purity to **5-c** and **7-c**. Wittig reaction of **5-c** and **7-c** with $Ph_3P{=}CH_2$ yielded **8** and **9** in about 70% yield each, and Suzuki coupling of 4-iodo-**2-c** and 1-pyreneboronic acid with $Pd(PPh_4)$ yielded 73% of **10**. Acetylation of the latter yielded 80% of an acetyl derivative, probably **11**.



8 Ar = 1-Naphthyl
9 Ar = 1-Pyrenyl
10 R=H
11 R=$COCH_3$

The two pyrenyl compounds **10** and **11** were found to be a mixture of two rotational isomers. For **10**, this is evidenced by four proton signals each for the *t*-butyl and internal methyl protons and four each for the $C(CH_3)_3$, the internal bridge and internal methyl carbons. Variable-temperature ^{1}H NMR over the range of 190 to 355 K for **10** resulted in peak movement, but no collapse of signals, so under these conditions, the isomers do not interconvert. This complexity is also present in the spectra of the acetyl derivative **11**, and because of this peak overlap, we are not certain whether **11** is mainly the 4-acetyl derivative shown or its 5-isomer. For the purpose of this paper, which isomer does not matter since observation of an opening rate increase on introduction of the acetyl group was the main objective. Full characterization of all of these compounds is provided in the Experimental Section. For comparison purposes, the acetyl derivative **12-c** was also synthesized.[15a,b] Since these two references report slightly different properties, we report our recent high-field NMR data, as well as UV−vis data (Tashiro's UV data can be found in ref 7) in the Experimental Section.

Thermal Ring Closing Reactions. The absorption spectra of five DHPs were characterized in order to use UV−vis absorption measurements to determine rate constants for the thermal closing reactions. The closed DHP isomers have absorption bands throughout the spectrum (Figure 1). When the DHP isomers were irradiated at long wavelengths (>500 nm), the CPD isomer was formed with an enhanced absorption in the UV (Figure 1). The absorption spectra of all compounds in the 300−450 nm region include the absorption by the DHP chromophore and of the fluorophore (e.g., pyrene, naphthalene) moieties appended to the DHP. The molar extinction coefficients for all the DHP isomers were determined at several wavelengths (see Supporting Information). The effect of substitution on the DHP is apparent from the changes in the position and molar absorptivity of the band with lowest energy. Parent **2-c** has an absorption maximum at 641 nm with a value of ϵ = 900 L mol^{-1} cm^{-1}, while the introduction of an acetyl substituent (**12-c**) led to a red shift of the absorption to 666 nm and an increase in ϵ to 2740 L mol^{-1} cm^{-1}. All compounds with a carbonyl containing substituent (**5-c**, **7-c**, and **11-c**) have absorption maxima between 663 and 671 nm, with molar absorptivity values between 2230 and 2860 L mol^{-1} cm^{-1}, while compounds **8-c** and **9-c** have an absorption maximum at 653 nm and a low ϵ value (744 and 780 L mol^{-1} cm^{-1}, respectively). Attaching a pyrene without the carbonyl spacer to the DHP moiety led to a small shift of the absorption band (648 nm) and slight increase in the ϵ value (1150 L mol^{-1} cm^{-1}). These results show that the decrease for the energy of the first excited singlet state (S_1) of the closed isomers and the increase in the absorption probability from S_0 to S_1 is primarily achieved with the introduction of the carbonyl containing substituent. The addition of the fluorescent moieties directly onto the ring or appended as an aroyl group did not change significantly the absorption properties of the DHPs.

The dark colored closed aroyldihydropyrenes **4-c**−**7-c** were all easily opened to the colorless cyclophanedienes **4-o**−**7-o** by irradiation of $CDCl_3$ solutions (for NMR experiments) or cyclohexane solutions (for UV−vis experiments) using ordinary tungsten household lamps with a >490 nm cutoff filter. Depending on concentration, 15−30 min irradiation gave >90% opening. Continued irradiation led to 100% ring opening, which was cleanly evidenced by ^{1}H NMR by the total disappearance of the internal methyl protons at about δ −3.8, while new CPD methyl proton signals appeared at about δ 1.5. This result was supported by UV−vis absorption measurements where prolonged irradiation above 500 nm led to the complete disappearance of the characteristic absorption above 600 nm for the closed isomers of the DHPs.

The kinetics for the thermal reaction of the open isomer back to the closed isomer were measured with absorption experiments. The kinetics were followed either for the changes of the absorption above 600 nm or for the changes in the band close to 500 nm. The kinetics followed a first-order behavior, and for this reason, a small absorption for the open isomer in the 500 nm band does not influence the value recovered for the rate constants of the thermal closing reactions. The rate constants were measured at various temperatures between 46 and 70 °C. The values for the activation energies (Table 1) were determined from Arrhenius plots (see Supporting Information), while the values for the activation enthalpies and entropies (Table 1) were determined from Eyring plots (see Supporting Information). The half-life of the open forms was calculated from the linear relationship determined in the Eyring plots (Table 1). Data for the acetyl derivative[7] **12-o**, the parent[16] **2-o**, and the benzo derivative[6,17] **13-o** are included for comparison.

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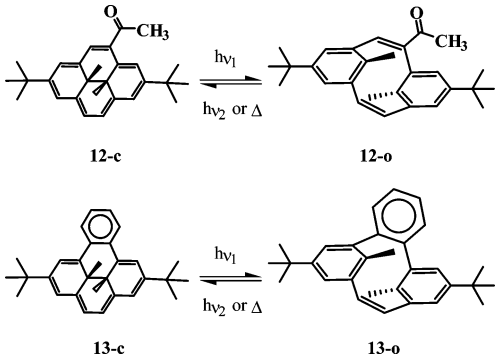
(16) Reference 7 gives E_{act} = 21.8 kcal mol^{-1}. Our best data, which start from synthetic fully open **1-o**, and follow the thermal closing using NMR integrations, yield 20.4 kcal mol^{-1} (Ayub, K. Ph.D. Thesis to be submitted, University of Victoria). Calculated $t_{1/2}$ (46 °C) values are then 3.12 h (Ayub) and 3.11 h (ref 7).

(17) Williams, R. V.; Edwards, W. D.; Mitchell, R. H.; Robinson, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 16207−16214.



As can be seen from the data, there are notable differences between E_{act} values for the various compounds. Clearly, the activation energies for the pyrenoyl (**7-o**), naphthoyl (**5-o**), and acetyl/pyrenyl (**11-o**) derivatives are similar to those of the parent (**2-o**), while the values found for benzoyl (**4-o**), anthranoyl (**6-o**), and acetyl (**12-o**) derivatives are more like the value for the benzo derivative **13-o**. Examination of the relative rates for thermal closing at 46 °C (shown as half-lives in Table 1) indicates them all to be acceptable. In contrast, introduction of the formyl group in to **1-o** to give **3-o** improved the photoopening but also increased the thermal closing rate by about 50-fold,[8] such that the half-life at room temperature was only 42 min. Our derivatives are thus much better and at room temperature (20 °C) have half-lives from 1.1 days (naphthoyl, **5-o**) to 6.7 days (anthranoyl, **6-o**); for reference, the parent (**2-o**) shows 2.3 days and benzo (**13-o**) 7.2 days. We are not yet in a position to fully understand exactly what determines the barrier for the thermal closing reaction,[17] but it is interesting that the anthranoyl compound **5-o** has the highest barrier and is the one compound in the series for which restricted rotation is observed for the DHP form, **5-c**. The open CPD form **5-o** does not appear to show any restricted rotation at room temperature, and possibly the additional strain energy to achieve this rotation in the closed form plays a roll in the barrier for the overall thermal reaction. The negative activation entropies suggest a lower degree of freedom in the transition state as expected for a unimolecular process with partial bond formation. It is worth noting that compounds with a lower activation enthalpy have a higher entropy of activation when compared to the compounds with higher activation enthalpies.

Irradiation with broad-band visible light of the non-carbonyl compounds **8**−**10** did not show any significant conversion to the open form, possibly because thermal and photochemical closing was occurring as fast as opening and so no thermal reactions were measured for these compounds.

Quantum Yields for Ring Opening Photoreactions. The ring opening quantum yields for all compounds were measured using Benzo-DHP **12-c** as a standard (Table 2). This method made it possible to irradiate the samples at long wavelengths, a procedure previously shown to be necessary because of the small absorption of the CPD isomers at shorter wavelengths.[3,11] Previous work showed that the low ring opening quantum yield of the parent DHP could be increased by a factor of 2.5 with the addition of an acetyl group at the 4-position (**12-c**).[3] For this reason, we chose a carbonyl group as the bridging group between the DHP and naphthalene or pyrene moieties. The ring opening quantum yields of the naphthalene (**5-c**) and pyrene (**7-c**) substituted compounds increased by a factor of about 2.4 compared to that of acetyl-DHP **12-c**. Replacement of the carbonyl group with an alkene (**8-c** and **9-c**) led to a reduction of the ring opening quantum yield (note that these experiments were performed at single wavelength and to low conversion). Direct attachment of the pyrene to the DHP ring (**10-c**) decreased the opening quantum yield when compared to that for the parent DHP **2-c**. The higher quantum yield was recovered if an acetyl group was added to compound **10-c** to form **11-c**. Within experimental errors, the ring opening quantum yields were the same for aerated solutions and solutions that were deoxygenated, suggesting that the ring opening reaction occurs from the singlet excited state as previously assigned.[3]

The photophysics of DHPs are different from the behavior observed for other photochromic systems because the lifetimes for the singlet excited states for the closed and open forms are in the nanosecond time domain,[3,11] while picosecond lifetimes are observed for most photochromic systems, such as spirooxazines, fulgides, and diarylethenes.[18] A recent theoretical study[19] showed that the low efficiency for the ring opening reaction is due to the complexity of the excited states involved. The reaction channel leading to the ring opening process is quenched by

TABLE 1. Values for the Activation Energy, Enthalpy, and Entropy and the Calculated Half-Life at 46 °C Obtained from the Arrhenius and Eyring Plots[a] for the Thermal Reaction of the Open to the Closed Isomer

compound	E_{act} kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}	$t_{1/2}$ (46°C) h
4-o (benzoyl)[b]	24 ± 1	23 ± 1	−6 ± 3	4.4
5-o (naphthoyl)[c]	20.2 ± 0.8	19.6 ± 0.8	−15 ± 2	1.5
6-o (anthranoyl)[d]	26 ± 1	26 ± 1	2 ± 4	4.0
7-o (pyrenoyl)[e]	20.5 ± 0.2	19.8 ± 0.3	−14.8 ± 0.8	1.9
11-o (acetyl,pyrenyl)[f]	20 ± 2	19 ± 2	−17 ± 5	2.4
2-o (parent)[g]	20.4	19.8	−15	3.1
12-o (acetyl)[h]	24.4			1.9
13-o (benzo)[i]	24.6	23.9	4	5.8

[a] Errors correspond to statistical errors from the linear fits of the Arrhenius or Eyring plots. For measurements at more than one wavelength, rate constants were averaged. [b] Kinetics measured at 489 and 658 nm. [c] Kinetics measured at 508 and 675 nm. [d] Kinetics measured at 489 and 658 nm. [e] Kinetics measured at 610 and 666 nm. [f] Kinetics measured at 671 nm. [g] See ref 16. [h] From ref 7. [i] From ref 6, and see also ref 17.

TABLE 2. Ring Opening Quantum Yields[a] Measured in Cyclohexane Using Benzo-DHP 13 as a Standard with Quantum Yield of 0.042[3]

compound	$(\phi_{DHP \rightarrow CPD})/10^{-3}$
2-c	1.5 ± 0.1[b]
13-c	42 ± 2[b]
12-c	3.8 ± 0.5[b]
5-c	9.2 ± 0.7 (4)
7-c	9.1 ± 0.8 (2)
8-c	3.0 ± 0.2 (2)
9-c	1.6 ± 0.2 (2)
10-c	0.7 ± 0.1 (2)
11-c	7.0 ± 0.4 (2)

[a] Errors correspond to standard deviations from independent experiments. The number of experiments are indicated in parentheses. [b] From ref 3.

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internal conversion to the lower excited state, which is nonreactive. The complex trends observed for the ring opening quantum yields for substituted DHPs[3,11] are probably due to subtle changes in the energies of the various excited states involved. Addition of the naphthoyl (**5-c**) and pyrenoyl (**7-c**) substituents enhanced the ring opening quantum yield without a decrease in the half-life for the thermal back reaction from the open to the closed form, leading to more efficient photoswitching. It is interesting to note that attachment of an aromatic moiety directly onto the DHP framework is counter productive, leading to a marked decrease of the ring opening quantum yield for **10-c**, which can be partially recovered by adding an acetyl substituent at the opposite site of the DHP ring (**11-c**). These results show that the rational design of substituted DHPs to increase their photochromicity is at this point not possible due to the limited understanding of the mechanism for photoswitching.

Fluorescence. Two excitation wavelengths are of relevance for the fluorescence experiments. DHPs have been shown to have a sharp fluorescence above 600 nm,[3,11] and excitation at 470 nm has sufficient energy to excite only the S_1 state of the DHP without exciting either the pyrene or naphthalene moieties. The excited states of naphthalene and pyrene can be reached when the molecules are excited at shorter wavelengths (260−350 nm).

The design feature for the DHPs with fluorescent moieties was the following: When the molecules are excited at 470 nm, only the emission of the DHP above 600 nm can be observed. In contrast, the emission of pyrene or naphthalene may be observable when the compounds are excited at short wavelengths. In the case of the DHP isomers, we would not expect any emission from naphthalene or pyrene because the S_1 state of DHP (<45 kcal/mol) is lower in energy when compared to the S_1 states of naphthalene (92 kcal/mol) and pyrene (77 kcal/mol)[20] and fast intramolecular energy transfer would be expected from the excited states of naphthalene and pyrene to the lower energy level of the DHP. However, the energy of the CPD isomers is much higher (e.g., 70−84 kcal/mol for [*e*]-annelated CPDs)[11] and is comparable to the excited state energies for the fluorescent moieties. In this case, an emission characteristic for naphthalene and pyrene could be observed if the CPD moiety did not act as a quencher. Therefore, the expectation was that on−off cycling for the emission above 600 nm would be mirrored by an off−on cycling for the emission of either the naphthalene or pyrene moieties.

Switching of the DHP emission above 600 nm when the DHP isomers were opened to the CPD isomers was observed (Figure 2 for **5-c**). The conversion from the DHP isomer to the CPD isomer was not complete, leading to a residual emission from the DHPs that were not opened. The range for the emission change between the completely closed form and the residual emission for the photostationary state depends on factors such as the ring opening quantum yields, the magnitude of the thermal reversion rate constants, and the time of irradiation used in the experiment. The changes observed for the emission above 600 nm show that fluorescence is a useful diagnostic tool to follow switching for DHPs. The major advantage in following the emission of the DHP closed form is that the fluorescence occurs at wavelengths where the photoswitch does not absorb, avoiding the possibility of reabsorption of the emitted light by the photoswitch. In addition, most materials, which maybe used as devices, such as polymers or films, are unlikely to have any appreciable absorption in the 600−700 nm region.

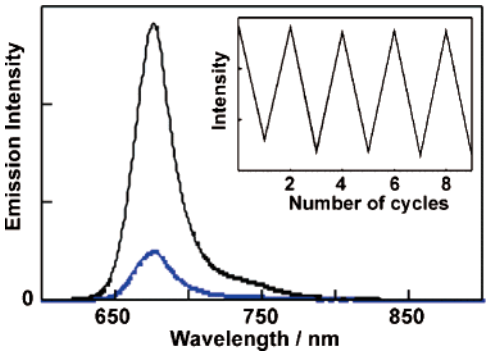

FIGURE 2. Emission of the DHP **5-c** in cyclohexane (λ_{ex} = 470 nm and λ_{em} = 676 nm, top spectrum, black) and the residual emission when the solution was irradiated above 590 nm (bottom spectrum, blue). The inset shows the cycling of the DHP emission of **5-c** after irradiation with visible light followed by irradiation with UV light.

Emission was also monitored by exciting **5-c** and **7-c** at shorter wavelengths. No emission was observed for the naphthoyl-DHP **5-c**, but an emission was observed for the pyrenoyl-DHP **7-c**. This emission occurred in the same spectral region as the fluorescence observed for pyrenecarboxylic acid in cyclohexane. Cycling between the DHP−CPD isomers of **7** led to a gradual and constant increase of the emission monitored at 383 nm. In addition, the intensity of the emission of **7** for solutions of equal concentrations was different for compounds prepared in different syntheses. These results suggest that a very fluorescent pyrene impurity is present in the samples of **7**. Attempts to identify this impurity by HPLC failed. From the analysis of the absorption spectra in the HPLC experiments, the samples seem pure (>99.5%). However, from fluorescence detection on the HPLC, a small shift in the retention time is observed, which could indicate the presence of an impurity that is highly fluorescent. In addition, the gradual increase of the emission at 383 nm during the cycling between the DHP and CPD isomers suggests that **7** is not stable to irradiation. No formation of decomposition products was observed by monitoring the NMR spectra of irradiated samples. It is important to note that fluorescence is much more sensitive than NMR, and the fact that decomposition is observed with the former technique suggests that the products formed are in small quantities but highly fluorescent.

These results show that the use of naphthalene and pyrene as a fluorescence moiety to follow the switching of the DHPs is not suitable, despite both substituents leading to an increase in the ring opening quantum yields without a slowdown of the thermal reversion reaction. One of the problems is that very small amounts of impurities (≤0.5%) overwhelmed the emission from the switch. These impurities are formed by a decomposition of the DHP, leading to a nonidentified photoproduct in very small yields. A second problem with using these chromophores is that their emission spectrum overlaps with the absorption spectrum of the closed form of the DHPs, leading to self-absorption of the emission and potential switching of the DHP. The design for future work with fluorescence DHPs will include fluorescent moieties that emit between 500 and 600 nm where the closed form of the DHP has minimal absorption.

(20) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd revised and expanded ed.; Marcel Dekker, Inc.: New York, 1993.

Conclusions

Several dihydropyrenes with fluorescent moieties were synthesized with the dual objective of enhancing the photochromic properties of these compounds and to establish the suitability of using fluorescence to follow the photoswitching between the open and closed forms of dihydropyrenes. The photochromicity of dihydropyrenes was enhanced with the addition of a carbonyl substituent to the 4-position of the dihydropyrene framework without decreasing the half-life for the thermal isomerization of the open isomer of these compounds. The aroyl substituent was mostly responsible for the enhanced ring opening quantum yields. The addition of fluorescent naphthyl or pyrenyl substituents was not suitable for the detection of the photoswitching between the open and closed forms of the dihydropyrenes because of the formation of very low level, but highly emissive, impurities. However, the emission of the closed form of the dihydropyrenes in the spectral region above 600 nm was shown to be an excellent monitoring method for the photoswitching. Therefore, fluorescence of dihydropyrenes even in the absence of appending emissive moieties will be the method of choice to follow the photoswitching of dihydropyrenes because of the sensitivity of fluorescence when compared to absorption measurements.

Experimental Section

Syntheses: General conditions and spectral assignment methods are given in the Supporting Information, as well as compound numbering for the NMR assignments.

4-Benzoyl-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene 4-c. Benzoyl chloride (0.5 mL, 4 mmol) and then anhydrous $AlCl_3$ (ca. 20 mg) were added under Ar to a stirred solution of dihydropyrene **2-c**[6] (50 mg, 0.16 mmol) in dry CH_2Cl_2 (25 mL) at 20 °C. After stirring for 6 h, ice−water was added to the deep blue solution, and then the organic layer was washed with 0.25 M aq KOH and water and then was dried and evaporated. The residue was chromatographed over neutral alumina using hexane/CH_2Cl_2 (1:1) as eluant. Eluted first was green unchanged **2-c**. Eluted second (a brown band) was product **4-c**: 35 mg (50%), dark greenish brown crystals from methanol, mp 192−194 °C (no lit. mp given[7]); ^{1}H NMR δ 8.95 (d, J = 1.0 Hz, 1H, H-3), 8.61 (s, 1H, H-5), 8.58 (s, 1H, H-6), 8.56 (s, 1H, H-8), 8.55 (s, 1H, H-1), 8.54 (*AB*, J = 7.7 Hz, 1H, H-9), 8.49 (A*B*, 1H, H-10), 7.91−7.89 (m, 2H, H-2′,6′), 7.62−7.59 (m, 1H, H-4′), 7.50−7.47 (m, 2H, H-3′,5′), 1.66 (s, 9H, 7-C(CH_3)$_3$), 1.55 (s, 9H, 2-C(CH_3)$_3$), −3.83 (s, 3H, 10b-CH_3), −3.84 (s, 3H, 10c-CH_3); ^{13}C NMR δ 199.5, 148.9 (C-2), 146.5 (C-7), 141.0 (C-1′), 139.0 (C-10a), 136.8 (C-10d), 136.1 (C-3a), 134.6 (C-5a), 132.5 (C-4′), 130.6 (C-2′,6′), 129.6 (C-4), 128.5 (C-3′,5′), 124.9 (C-9), 124.7 (C-5), 123.8 (C-10), 123.2 (C-6), 122.9 (C-8), 121.5 (C-1), 120.3 (C-3), 36.5 (2-*C*(CH_3)$_3$), 36.2 (7-*C*(CH_3)$_3$), 32.1 (7-C(*C*H_3)$_3$), 31.9 (2-C(*C*H_3)$_3$), 30.9 (C-10b), 29.5 (C-10c), 15.0 and 14.9 (10b,c-CH_3); UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 343 (62300), 394 (43200), 489 (9070), 657 (2090) [lit.[7] ϵ = 53000, 35000, 8600, 1900]; HRMS *m*/*z* calcd for $C_{33}H_{36}O$ 448.2777, found 448.2766. Anal. Calcd: C, 88.35; H, 8.09. Found: C, 87.99; H, 8.23.

The Open Isomer 4-o. Irradiation of an NMR sample in $CDCl_3$ with visible light (see general photochemistry section) until the color disappeared gave a solution of **4-o**: ^{1}H NMR δ 7.87 (∼d, J = 7.3 Hz, 2H), 7.51 (∼t, J = 7.3 Hz, 1H), 7.42 (∼t, J = 7.3 Hz, 2H), 7.16 (s, 1H), 6.78, 6.76, and 6.73 (3s, 3H), 6.50 (s, 1H), 6.41 and 6.40 (AB, J = 11.3 Hz, 2H), 1.56 and 1.50 (s, 3H each, 10b,c-CH_3), 1.25 and 1.14 (s, 9H each, 2,7-C(CH_3)$_3$); ^{13}CNMR δ 197.9, 152.2, 150.7, 144.0, 143.8, 143.0, 140.7, 138.5, 138.1, 137.7, 137.4, 136.0, 133.3, 132.7, 132.4, 129.7, 128.5, 124.8, 124.6, 123.49, 123.46, 34.3, 31.54, 31.47, 20.1, 19.4.

2,7-Di-*tert*-butyl-4-(1-naphthoyl)-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene 5-c. Using the procedure for **4-c**, from 1-naphthoyl chloride (0.3 mL, 2 mmol) and dihydropyrene **2-c** (57 mg, 0.17 mmol) for 2 h was obtained 81 mg (97%) of **5-c** as dark brown crystals from methanol, mp 196−197 °C: ^{1}H NMR δ 9.39 (d, J = 1.0 Hz, 1H, H-3), 8.61 (br s (b = half-width ∼ 2.57 Hz), 1H, H-5), 8.57 (br s, 1H, H-6), 8.56 (br s, 1H, H-1), 8.54 (d, 1H, J = 7.9 Hz, H-10), 8.48 (d, 1H, J = 7.9 Hz, H-9), 8.47 (br s, 1H. H-8), 8.44 (dm, 1H, J_d = 8.3 Hz, H-8′), 8.06 (dm, 1H, J_d = 8.3 Hz, H-2′), 7.98 (dm, 1H, J_d = 8.3 Hz, H-5′), 7.63 (dd, J = 7.0, 1.3 Hz, 1H, H-4′), 7.54 (td, J = 6.8, 1.2 Hz, 1H, H-6′), 7.49 (dd, J = ∼7 Hz, 1H, H-3′), 7.47 (td, J = 6.8, 1.4 Hz, 1H, H-7′), 1.61 (s, 9H, 7-C(CH_3)$_3$), 1.55 (s, 9H, 2-C(CH_3)$_3$), −3.81 (s, 3H, 10b-CH_3), −3.84 (s, 3H, 10c-CH_3); ^{13}C NMR δ 201.0 (C═O), 150.4 (C-2), 146.3 (C-7), 140.4 (C-1′), 139.8 (C-10a), 137.0 (C-3a), 136.8 (C-5a), 134.5 (C-10d), 134.1 (C-8b′), 131.5 (C8a′), 131.4 (C-2′), 129.9 (C-3b), 128.9 (C-4′), 128.6 (C-5′), 127.5 (C-7′), 126.6 (C-6′), 126.3 (C-8′), 126.1 (C-5), 125.3 (C-10), 124.9 (C-3′), 123.9 (C-8), 123.8 (C-9), 123.4 (C-6), 121.6 (C-1), 120.4 (C-3), 36.7 (2-*C*(CH_3)$_3$), 36.1 (7-*C*(CH_3)$_3$), 32.0 (7-C(*C*H_3)$_3$), 31.9 (2-C(*C*H_3)$_3$), 31.2 (C-10b), 29.4 (C-10c), 15.1 (10c-CH_3), 14.9 (10b-CH_3); IR (KBr) ν 2961 (s), 1640 (s), 1506 (m), 1460 (m), 1343 (m), 1228 (s), 1196 (m), 1108 (m), 886 (s), 781 (s), 672 (m) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 289 (9920), 343 (41100), 399 (35700), 492 (7200), 607 (541), 663 (2230); CI MS *m*/*z* 499 (MH^+); HRMS *m*/*z* calcd for $C_{37}H_{38}O$ 498.2923, found 498.2922. Anal. Calcd: C, 89.11; H, 7.68. Found: C, 88.69, H, 7.94.

The Open Isomer 5-o. Irradiation of an NMR sample in $CDCl_3$ with visible light (see general photochemistry section) until the color disappeared gave a solution of **5-o**: ^{1}H NMR δ 8.32 (d, J = 7.7 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.70 (∼d, J = 7.3 Hz, 1H), 7.60−7.48 (m, ∼3H), 7.19 (s, 1H), 6.77, 6.73, 6.72, 6.65 (4s, 4H), 6.40 and 6.38 (AB, J = 11.2 Hz, 2H), 1.51 and 1.50 (s, 3H each, 10b,c-CH_3), 1.23 and 1.14 (s, 9H each, 2,7-C(CH_3)$_3$); ^{13}CNMR δ 199.8, 152.1, 150.6, 145.9, 145.3, 144.0, 141.0, 138.0, 137.7, 137.4, 136.6, 136.0, 134.0, 133.4, 132.6, 131.2, 128.7, 127.5, 127.4, 126.6, 125.8, 124.98, 124.96, 124.65, 124.56, 124.47, 123.8, 34.28, 34.26, 31.4, 31.3, 20.2, 19.3.

4-(9-Anthranoyl)-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene 6-c. 9-Anthracenecarboxylic acid (129 mg, 0.58 mmol) and oxalyl chloride (0.2 mL, 2 mmol) in dry CH_2Cl_2 (30 mL) were stirred under reflux under argon for 6 h. The solvent and excess oxalyl chloride were removed under vacuum. Dry CH_2Cl_2 (30 mL) was then added to the yellow residue, followed by dihydropyrene **2-c** (50 mg, 0.14 mmol) and anhyd $AlCl_3$ (∼20 mg). The deep blue solution was stirred for 4 h at 20 °C, and then ice−water was added. The organic layer was separated, washed with aq 10% KOH, water, and then was dried and evaporated. The residue was chromatographed over alumina (neutral) using hexane/dichloromethane (1:1) as eluant. Eluted first was any unchanged **2-c**. Eluted second was 61 mg (80%) of **6-c** as dark brown crystals from methanol: mp 222−224 °C; ^{1}H NMR δ 10.5 (br s ∼30 Hz width, 1H, H-3), 8.64 (s, 2H, H-1,10′), 8.60 (br s ∼30 Hz width, 1H, H-5), 8.53 and 8.48 (AB, J = 8 Hz, H-9,10), 8.52 (s, 1H, H-1), 8.24 (br s ∼30 Hz width, 1H, H-6), 8.11 (d, J = 8.6 Hz, 2H, H-4′,5′), 7.98 (d, J = 9.0 Hz, 2H, H-1′,8′), 7.46−7.43 (m, 2H, H-3′,6′), 7.28−7.25 (m, 2H, H-2′,7′), 1.75 (v br s, 9H, 2-C(CH_3)$_3$), 1.56 (s, 9H, 7-C(CH_3)$_3$), −3.81 and −3.86 (s, 3H each, 10b,c-CH_3). In d_8-toluene, at 380 K, the broad signals for H-3, H-5, H-6, and the 2-*t*-Bu all sharpen and likewise in $CDCl_3$ at 210 K: ^{13}C NMR δ ∼203, 152.4 (br), 146.1, 140.8, 138.33, 137.1, 136.7, 134.7, 131.6, 129.3, 128.8, 128.2, 127.5 (br), 126.5, 126.1, 125.9, 125.6, 124.8, 124.1, 123.8, 121.7, 120.7 (br), 36.9 (br, -*C*(CH_3)$_3$), 36.0 (-*C*(CH_3)$_3$), 32.1 (br,-C(*C*H_3)$_3$), 32.0 (−C(*C*H_3)$_3$), 31.6 and 29.4 (C-10b,c), 15.3 and 15.0 (10b,c-CH_3); IR (KBr) ν 2961 (s), 1639 (s), 1444 (m), 1347 (m), 1233 (m), 1196 (s), 1113 (m), 883 (s), 846 (w), 731 (s), 672 (m) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 255 (96800), 347 (22500), 367 (21000), 388 (20800), 406

(31000), 493 sh (5200), 513 (5540), 676 (3050); CI MS *m/z* 549 (MH^+); HRMS *m/z* calcd for $C_{41}H_{40}O$ 548.3079, found 548.3083. Anal. Calcd: C, 89.74; H, 7.35. Found: C, 88.79, H, 7.48. This compound is the least stable of **4-c**−**7-c** (especially in solution) and was not possible to free completely of oxidized impurity.

The Open Isomer 6-o. Irradiation of an NMR sample in $CDCl_3$ with visible light (see general photochemistry section) until the color disappeared gave a solution of **6-o**: ^{1}H NMR δ 8.55−8.53 (m, ∼1H), 8.10−7.97 (m, ∼4H), 7.57−7.43 (m, ∼5H), 7.14−6.73 (m, ∼3H), 6.50−6.30 (m, ∼3H), 1.47 and 1.46 (s, 3H each, 10b,c-CH_3), 1.18 and 1.17 (s, 9H each, 2,7-C(CH_3)$_3$); ^{13}CNMR δ 201.3, 152.1, 150.4, 145.2, 144.3, 141.0, 140.8, 138.1, 137.2, 136.0, 135.0, 133.4, 132.9, 132.5, 131.4, 129.7, 129.1, 129.0(*), 128.8, 128.5, 125.8, 125.7(*), 125.4, 125.3, 123.5, 123.2. 34.4, 34.2, 31.4 (both C(*C*H_3)$_3$), 20.4, 19.2; (*) = small peaks also underneath.

2,7-Di-*tert*-butyl-4-(1-pyrenoyl)-*trans*-10b,10c-dimethyl-10b,-10c-dihydropyrene 7-c. Using the procedure described for **6-c** above, 1-pyrenecarboxylic acid (286 mg, 1.16 mmol), oxalyl chloride (0.2 mL, 2 mmol) in dry CH_2Cl_2 (30 mL), and then dihydropyrene **2-c** (100 mg, 0.291 mmol) and $AlCl_3$ (∼40 mg) in CH_2Cl_2 (30 mL) at 20 °C for 4 h yielded 133 mg (80%) of brown crystals of **7-c**: mp 213−214 °C; ^{1}H NMR δ 9.52 (d, J = 1.1 Hz, 1H, H-3), 8.65 (d, J = 9.3 Hz, 1H, H-10′), 8.59 (s, 1H, H-1), 8.575 (s, 1H, H-6), 8.570 (s, 1H, H-5), 8.56 (d, J = 7.9 Hz, 1H, H-10), 8.51 (d, 1H, J = 7.9 Hz, H-9), 8.40 (s, 1H, H-8), 8.27 (dd, J = 7.7, 1.0 Hz, 1H, H-6′), 8.21 (d, J = 8.9 Hz, 1H, H-5′), 8.20 (d, J = 7.85 Hz, 2H, H-3′,8′), 8.16 (d, J = 7.85 Hz, 1H, H-2′), 8.15 (d, J = 9.9 Hz, 1H, H-4′), 8.05 (dd, J = 8.05 Hz, 1H, H-7′), 8.04 (d, J = 9.3 Hz, 1H, H-9′), 1.57 (s, 9H, 7-C(CH_3)$_3$), 1.55 (s, 9H, 2-C(CH_3)$_3$), −3.75 (s, 3H, 10b-CH_3), −3.78 (s, 3H, 10c-CH_3).;^{13}C NMR δ 201.4 (C═O), 150.6 (C-2), 146.3 (C-7), 139.9 (C-3a/10a), 137.2, 137.1 (C-10a/3a), 136.8 (C-5a/10d), 134.6 (C-10d/5a), 133.3, 131.5, 131.1, 130.2 (C-4), 130.1, 129.3 C-3′/5′/8′), 129.0 (C-7′), 128.1 (C-2′), 127.6 (C-1′), 126.54 (c-5/6,9′), 126.53 (c-5/6,9′), 126.2 (C-6′), 126.0 (C-3′/5′/8′), 125.39 (C-10/10′), 125.37 (C-10′/10), 125.2, 124.9, 124.3 (C-3′/8′), 124.0 (C-8), 123.8 (C-9), 123.5 (C-6/5), 121.6 (C-1), 120.6 (C-3), 36.7 (2-*C*(CH_3)$_3$), 36.1 (7-*C*(CH_3)$_3$), 32.0 (7-C(*C*H_3)$_3$), 31.9 (2-C(*C*H_3)$_3$), 31.3 (C-10b), 29.4 (C-10c), 15.2 (10c-CH_3), 15.0 (10b-CH_3); IR (KBr) ν 2962 (s), 1633 (s), 1595 (m), 1505 (m), 1383 (m), 1343 (m), 1249 (m), 1220 (s), 1114 (m), 1066 (m), 1016 (m), 940 (w), 887 (s), 840 (s), 781 (m) 729 (s) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 234 (50600), 240 (50700), 274 (26900), 341 (57500), 401 (44900), 498 (7820), 665 (2,600); HRMS *m/z* calcd for $C_{43}H_{40}O$ 572.3079, found 572.3085.

The Open Isomer 7-o. Irradiation of an NMR sample of **7-c** in $CDCl_3$ with visible light (see general photochemistry section) until the color disappeared gave a solution of **7-o**: ^{1}H NMR δ 8.60 (d, J = 9.3 Hz, 1H), 8.27−8.05 (m, 8H), 7.20 (s, 1H), 6.82, 6.78, 6.73, 6.64 (4s, 4H), 6.41 and 6.40 (AB, J = 8.7 Hz, 2H), 1.58 and 1.56 (s, 10b,c-CH_3), 1.22 and 1.12 (s, 2,7-C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 200.2, 152.2, 150.6, 146.1, 145.7, 144.0, 141.0, 138.1, 137.4, 136.7, 136.1, 134.5, 133.4, 133.1, 132.6, 131.4, 131.0, 129.9, 129.2, 129.1, 127.5, 126.7, 126.6, 126.2, 126.1, 125.14, 125.08, 125.0, 124.9, 124.7, 124.2, 123.4, 123.4, 34.3, 34.3, 31.3, 27.1, 20.3, 19.3.

1-[4-(2,7-Di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrenyl)]-1-(1-naphthyl)ethene 8-c. Butyllithium (0.28 mL, 0.7 mmol in hexane) was added under argon to a stirred suspension of methyltriphenylphosphonium bromide (Aldrich, 98%) (179 mg, 0.5 mmol) in dry THF (25 mL). The yellow solution was stirred for 5 min at 20 °C, and then dihydropyrene **5-c** (50 mg, 0.10 mmol) in dry THF (10 mL) was added. The solution was refluxed for 1 h under argon, cooled, and then water was added. The product was extracted using dichloromethane and was then washed, dried, and chromatographed to give 35 mg (70%) of yellowish green crystals of **8-c**: mp 176−177 °C; ^{1}H NMR δ 8.86 (d, J = 1.3 Hz, 1H, H-3), 8.45 (d, J = 1.3 Hz, 1H, H-6), 8.42 (d, J = 1.3 Hz, 1H, H-1), 8.41 (s, 1H, H-5), 8.40 (d, J = 1.3 Hz, 1H, H-8), 8.37 (s, 2H, H-9,10), 8.30 (ddd, J = 8.6, 1.9, 0.9 Hz, 1H, H-8′), 7.83 (dm, J = ∼8 Hz, 1H, H-5′), 7.82 (dm, J = ∼8 Hz, 1H, H-4′), 7.62 (dd, J = 7.1, 1.5 Hz, 1H, H-2′), 7.48 (dd, J = 8.3, 7.1 Hz, 1H, H-3′), 7.34 (ddd, J = 8.6, 6.8, 1.2 Hz, 1H, H-6′), 7.14 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H, H-7′), 6.065 and 6.063 (d, J = 2.4 Hz, 1H each, >C═CH_2), 1.62 (s, 9H, 7-C(CH_3)$_3$), 1.41 (s, 9H, 2-C(CH_3)$_3$), −3.89 (s, 3H, 10c-CH_3), −3.93 (s, 3H, 10b-CH_3). ^{13}C NMR δ 149.6 (>*C*═CH_2), 145.99 (C-2), 145.98 (C-7), 142.8 (C-1′), 137.3 (C-10a), 137.0 (C-10d), 136.3 (C-5a), 135.9 (C-4), 134.2 (C-8b), 132.7 (C-3a), 132.0 (C-8a), 128.5 (C-5′), 128.0 (C-4′), 127.2 (C-2′), 126.5 (C-8′), 125.9 C-7′), 125.74 (C-6′), 125.68 C-3′), 124.4 (C-5), 123.1 and 122.9 (C-9,10), 122.0 (═CH_2), 121.3 (C-8), 120.9 (C-6), 120.8 (C-1), 120.4 (C-3), 36.2 (2-*C*(CH_3)$_3$), 36.1 (7-*C*(CH_3)$_3$), 32.1 (7-C(*C*H_3)$_3$), 31.9 (2-C(*C*H_3)$_3$), 30.5 (C-10b), 29.9 (C-10c), 15.1 (10c-CH_3), 14.2 (10b-CH_3); IR (KBr) ν 2946 (s), 1435 (m), 1358 (m), 1230 (m), 1119 (m), 886 (m), 802 (m), 777 (s), 721 (m), 542 (m) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 288 (80400), 350 (43800), 389 (31900), 484 (6500), 653 (744); CI MS *m/z* 496 (M+); HRMS *m/z* calcd for $C_{38}H_{40}$ 496.3130, found 496.3126. Anal. Calcd: C, 91.88; H, 8.12. Found: C, 91.57; H, 8.23.

1-[4-(2,7-Di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrenyl)]-1-(1-pyrenyl)ethene 9-c. This compound was prepared from butyllithium (0.6 mmol), methyltriphenylphosphonium bromide (Aldrich, 98%) (160 mg, 0.45 mmol), dry THF (25 mL), and then dihydropyrene **7-c** (50 mg, 0.087 mmol) in dry THF (10 mL) exactly as described for **8-c** above. After chromatography, 35 mg (70%) of yellowish green crystals of **9-c** was obtained: mp 187−189 °C; ^{1}H NMR δ 8.92 (d, J = 1.2 Hz, 1H, H-3), 8.61 (d, J = 9.3 Hz, 1H, H-10′), 8.45 (d, J = 1.2 Hz, 1H, H-8), 8.42 (d, J = 1.2 Hz, 1H, H-1), 8.41 (s, 1H, H-5), 8.39 (s, 2H, H-9,10), 8.37 (br s, 1H, H-6), 8.15 (d, J = 7.9 Hz, 1H, H-3′), 8.14 (dd, J = 7.6, 1.1 Hz, 1H, H-6′), 8.10 (d, J = 7.9 Hz, 1H, H-2′), 8.06 and 8.05 (AB, J = 8.95 Hz, 2H, H-4′,5′), 8.03 (dd, J = 7.7, 1.0 Hz, 1H, H-8′), 7.93 (t, J = 7.7 Hz, 1H, H-7′), 7.80 (d, J = 9.3 Hz, 1H, H-9′), 6.22 (d, J = 2.0 Hz, 1H, >C═CH_aH$_b$), 6.18 (d, J = 2.0 Hz, 1H, >C═CH$_a$*H$_b$*), 1.60 (s, 9H, 7-C(CH_3)$_3$), 1.37 (s, 9H, 2-C(CH_3)$_3$), −3.85 (s, 3H, 10c-CH_3), −3.88 (s, 3H, 10b-CH_3); ^{13}C NMR δ 149.8 (>*C*═CH_2), 146.1 (C-2), 146.0 (C-7), 140.4 (C-1′), 137.3 and 137.0 (C-10a,10d), 136.3 (C-5a), 136.2 (C-4), 132.9 (C-3a), 131.7 (C-5a′), 131.2 (C-10d′), 130.8 (C-3a′), 129.0 (C-10a′), 127.72 (C-2′), 127.67 and 127.47 (C-4′,5′), 127.35 (C-9′), 126.1 (C-7′), 125.9 (C-10′), 125.4 (C-10b′), 125.21 (C-10c′), 125.19 (C-6′), 124.94 (C-3′), 124.93 (C-8′), 124.7 (C-5′), 123.2 and 123.0 (C-9,10), 122.8 (>C═*C*H$_2$), 121.4 (C-6), 121.0 (C-8), 120.9 (C-1), 120.5 (C-3), 36.2 (2-*C*(CH_3)$_3$), 36.1 (7-*C*(CH_3)$_3$), 32.1 (7-C(*C*H_3)$_3$), 31.9 (2-C(*C*H_3)$_3$), 30.5 (C-10b), 29.9 (C-10c), 15.1 (10c-*C*H_3), 14.3 (10b-*C*H_3); IR (KBr) ν 3042 (w), 2959 (s), 1437 (m), 1231 (m), 1119 (m), 845 (s) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 235 (37600), 242 (37600), 268 (20100), 278 (26100), 348 (59300), 391 (41600), 484 (6750), 653 (782); CI MS *m/z* 570 (M^+); HRMS *m/z* calcd for $C_{44}H_{42}$ 570.3287, found 570.3300.

2,7-Di-*tert*-butyl-4-(1-pyrenyl)-*trans*-10b,10c-dimethyl-10b,-10c-dihydropyrene 10-c. 4-Iodo-**2-c**[3] (46 mg, 0.1 mmol), 1-pyreneboronic acid (Aldrich, 50 mg, 0.2 mmol), and tetrakis(triphenylphosphine)palladium(0) (Aldrich, 5 mg) in THF (20 mL) were refluxed under argon for 2 h, cooled to room temperature, and then hexane was added. The organic layer was washed, dried, and evaporated. The residue was chromatographed on neutral alumina, using first hexane, which eluted a small amount of unchanged green iododihydropyrene. Hexane/benzene (6:1) then eluted the second bright green band to give 40 mg (73%) of the product **10-c**: mp 208−209 °C, which by NMR is a mixture of two approximately equal rotational isomers; ^{1}H NMR δ 8.60−7.75 (m, 16H), 1.70, 1.54, 1.40, and 1.35 (s, 9H each), −3.58, −3.59, −3.71 and −3.74 (s, 3H each); ^{13}C NMR δ 146.44, 146.37, 146.24, 146.19, 138.8, 137.9, 137.3, 137.1 (×2), 136.4, 136.0, 135.3, 134.6, 133.9, 133.7, 131.83, 131.82, 131.42, 131.40, 131.0, 130.9, 130.8, 130.2, 130.0, 129.5, 127.91, 127.88, 127.7, 127.5, 127.34, 127.27, 127.0, 126.5, 126.28, 126.25, 126.1, 125.3, 125.2 (>×2), 125.1, 125.0, 124.6, 124.3,

123.24, 123.22, 123.15, 123.11, 121.2, 121.1 (>×2), 120.9, 36.3 (×2), 36.2, 36.1, 32.2, 32.0, 30.6, 30.4, 30.1, 30.0, 15.3, 15.1, 14.9, 14.8; IR (KBr) ν 2962 (s), 1506 (m), 1460 (m), 1382 (m), 1360-(m), 1343 (m), 1231 (m), 884 (m), 843 (s), 755 (m), 668(m) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 233 (51200), 241 (68300), 264 (24900), 274 (29400), 346 (75500), 389 (49600), 483 (9930), 648 (1150); CI MS *m*/*z* 544 (M^+); HRMS *m*/*z* calcd for $C_{42}H_{40}$ 544.3130, found 544.3143. Anal. Calcd: C, 92.60; H, 7.40. Found: C, 92.34, H, 7.58.

4-Acetyl-2,7-di-*tert*-butyl-9-(1-pyrenyl)-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene 11-c. Acetic anhydride (1 mL) was added under argon to the pyrenyldihydropyrene **10-c** (33 mg, 0.061 mmol) in dried dichloromethane (25 mL). The solution was stirred at room temperature for 10 min, then boron trifluoride diethyl etherate (1 mL) was added. The solution was stirred under argon at room temperature for another 3 h, and then ice−water (20 mL) was added. The organic layer was separated, washed with aqueous 10% potassium hydroxide, water, and then was dried and concentrated. The residue was chromatographed over neutral aluminum oxide with hexane/dichloromethane (1:1) as eluant. Eluted first was a green band containing a small amount of starting **10-c**. Eluted second was a deep brown band which yielded 28 mg (80%) of dark brown crystals of **11-c**: mp 148−150 °C, which by NMR is a mixture of rotational isomers (see **10-c**); ^{1}H NMR δ 9.86−7.73 (m, 15H), 3.126, 3.124, 3.119, 3.115 (s, 3H total, $-COCH_3$), 1.71, 1.70, 1.35, 1.34 (s, 18H total, $-C(CH_3)_3$), −3.44 to −3.61 (8s, 6H total, 10c,10d-CH_3); ^{13}C NMR δ 202.6 and 202.4 (C═O), 151.7−120.8 (60 peaks), 36.9−36.1 (6 peaks), 33.5−29.5 (16 peaks), 15.9−14.3 (8 peaks); IR (KBr) ν 2962 (s), 2922 (s) 1661 (s), 846 (s) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 273 (30100), 348 (41300), 404 (55100), 487 (82300), 671 (2860); EI MS *m*/*z* 586 (M+); HRMS calcd for $C_{44}H_{42}O$ 586.3236, found 586.3234.

4-Acetyl-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene 12-c. This is a modified procedure from refs 15a,b. $BF_3{\cdot}Et_2O$ (1.2 mL) was added to a solution of **2-c** (345 mg, 1.00 mmol) in acetic anhydride (3 mL) at 20 °C, and the mixture was stirred for about 30 min (monitored by the disappearance of the fast moving DHP spot on TLC). The mixture was then poured on to crushed ice and extracted with dichloromethane. The organic layer was washed with satd $NaHCO_3$ soln, water, and then was dried and evaporated. The residue was chromatographed on silica gel using hexane to elute unchanged **2-c** and then hexane/ethyl acetate (1:1) to elute product, which yielded 180 mg (49%) of brownish-green crystals: mp 184−185 °C (lit. mp 185−187 °C,[15a] 183−185 °C[15b]); ^{1}H NMR (360 MHz) δ 9.79 (d, J = 1.0 Hz, 1H, H-3), 8.92 (s, 1H, H-5), 8.64 (s, 1H, H-6), 8.54 (s, 1H, H-1), 8.45 and 8.51 (AB, J = 7.8 Hz, 1H, H-9,10), 3.07 (s, 3H, 4-$COCH_3$), 1.69 and 1.68 (s, 9H each, 2,7-$C(CH_3)_3$), −3.93 and −3.94 (s, 3H each, 10b,c-CH_3); ^{13}C NMR (90.6 MHz) δ 202.1, 150.8, 146.0, 139.7, 136.5, 135.6, 134.8, 127.9, 125.1, 124.3, 123.6, 123.4, 123.1, 121.4, 120.6, 36.6, 35.9, 31.9, 30.84, 30.78, 28.1, 15.0, 14.5; UV−vis λ_{max} (ϵ_{max}, L mol^{-1} cm^{-1}, nm) 346 (37800), 395 (39500), 495 (7240), 666 (2740).

Photophysics and Kinetic Experiments. Details on solvent sources, HPLC procedures, and equipment description and settings for absorption and fluorescence measurements are described in the Supporting Information.

Irradiation Procedures for the Interconversion between the DHP and CPD Isomers. The photochemical conversion of the DHP isomer to the CPD isomer was achieved by using as the light source a 500 W household tungsten-halogen lamp (8500 lumens). A cutoff filter (λ > 490 nm or λ > 590 nm) and a 1 L beaker containing ice−water were placed between the light source and the fluorescence cell. The container with water was used to filter infrared emission from the light source, and ice was used to cool the water in the container. The distance between the light source and the sample cell was ca. 27 cm. The irradiation time with visible light was usually between 20 and 30 min.

Irradiation of the CPD isomers was performed by placing samples in a black box and irradiating them with a 3 W low-pressure Hg pencil light source (254 nm). The distance between the UV light source and the samples was ca. 5 cm. The UV light irradiation time was usually between 10 and 15 min.

Determination of the Thermal Decay Rate Constants for the CPD Isomers. DHP samples were irradiated by visible light to achieve a significant conversion to the CPD isomer. The kinetics for the thermal conversion of the CPD isomer into the DHP isomer were followed by absorption measurements either for the absorption band at the wavelengths above 600 nm or for the absorption close to 500 nm. The molar fraction (X) of CPD was calculated, and the first-order rate constants at various temperatures were obtained from plots of $\ln(X_t)$ versus time.

Determination of Molar Absorptivity Coefficients and Ring Opening Quantum Yield. Molar absorptivity coefficients were determined from absorption values for solutions with at least three different DHP concentrations (see Supporting Information for details). The ring opening quantum yields were determined using benzo-DHP **13-c** as a standard (0.042),[3] using a method adapted[3] from previous literature measurements[21] (see Supporting Information for details).

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Supporting Information Available: General synthetic experimental conditions, photophysical experimental conditions, compound numbering; molar absorption coefficients for compounds **5-c**, **7-c**, **8-c**, **9-c**, **10-c**, and **11-c**; thermal closing data for **4-o**, **5-o**, **6-o**, **7-o**, and **11-o**; VT NMR spectra for **6-c** and **10-c**; ^{1}H and ^{13}C NMR spectra for **5-c**, **7-c**, **8-c**, **9-c**, **10-c**, and **11-c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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