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Oligothiophene Functionalized Dimethyldihydropyrenes I: Syntheses and Photochromicity

Stephen G. Robinson, Vittorio A. Sauro, and Reginald H. Mitchell*

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

regmitch@uvic.ca

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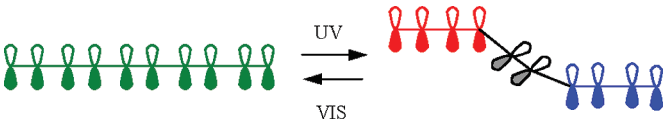

The syntheses of 2,7-di-*tert*-butyldimethyldihydrobenzo[*e*]pyrenes with thienyl (**6**), terthienyl (**7**), and pentathienyl (**14**) side chains at the 4,5- positions, ter- and pentathienyl side chains at the 4-position with ter- (**39**) and pentathienylcarbonyl (**40**) side chains at the 10- and 11-positions, 2-naphthoyl-7-*tert*-butyldimethyldihydropyrenes with ter- (**53**), penta- (**54**), and septithienyl (**55**) side chains at the 4,9-positions are described. These compounds are all photochromic and open to the corresponding cyclophanedienes with long wavelength (> 490 nm) light, and as such, the conjugative path could change considerably, making them suitable to investigate as potentially switchable conducting molecules. In this paper, the syntheses and the photochemical and thermal isomerizations are studied; in the accompanying paper, the electrochemical and conductive properties are studied. Here, a comparison of the relative opening rates to that of the benzo[*e*]pyrene **4** (with no thienyl substituents) is made, and all of the above photochromes show considerably enhanced photo-opening of the DHPs to the CPDs. As examples, **14**, **40**, and **54** were cycled between the open and closed forms, and no decomposition was observed; however, when **54** was irradiated for 40 h with 254 nm light, some radicals did form, which enhanced the thermal closing rate, and so extensive irradiation with short wave UV is better avoided. The thermal closing reactions were also studied, and all of the above compounds close faster than benzo-CPD **4′**, though for the highly photochromic ter- and pentathienyl benzo-CPDs **39′** and **40′**, the rate was not too enhanced from that of **4′** and so are probably the best compromise between fast photochromicity and slow thermal reversion.

Introduction

The idea of using a photochromic compound to control electrical conductivity in a conducting polymer was first proposed by Lehn et al.[1] By synthesis of bispyridinium dithienylethenes, they were able to demonstrate a prototype of a light-triggered switchable molecular wire. Irie[2] attached oligothiophenes (as the molecular wire) to the very robust dithienylethene switch[3] *but* found that the ring-opening quantum yield of the switch dramatically decreased as the number of thiophene units increased.[4] In 1999, Irie reported[5] a diarylethene switch directly in the main chain of a poly(9,9-dialkylfluorene). In the polymer, the electrical conductivity in the closed form was 2.3 times that in the open form. When doped with iodine, the conductivity of the doped form increased some 12 000× but, unfortunately then, photochromism was not observed. Shortly afterward, we reported[6] the backbone photochromic polymer **1**, as a prototype conducting main chain photochromic conjugated polymer. However, because of the rather poor efficiency[7] of the ring-opening reaction of the parent dihydropyrene **2**, the observed

*To whom correspondence should be addressed. Phone: 250-598-7679. Fax: 250-721-7147. E-mail: regmitch@uvic.ca.

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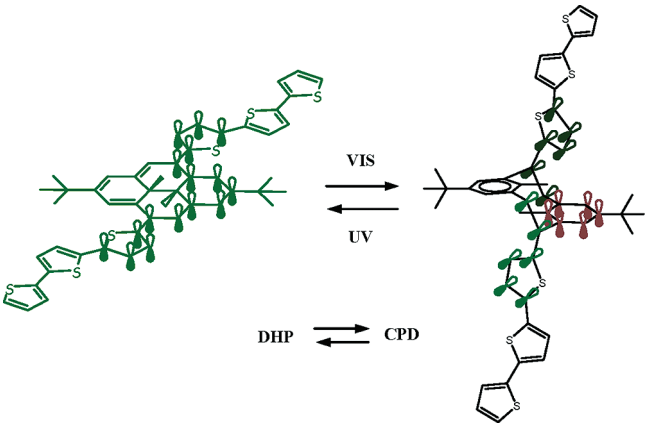
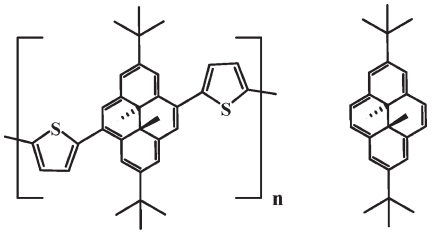


FIGURE 1. Change in conjugation along the backbone when the dihydropyrene (DHP) form is converted to the cyclophanediene (CPD) form.

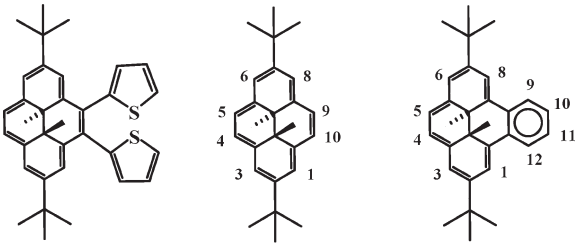
change in conductivity was rather small (1.5×). Other researchers have more recently carried out work on a dithienylethene quinoline polymer[8] and on single molecules between gold electrodes[9] or attached to nanotubes.[10] However, since we have now very much improved the switching ability of dihydropyrenes,[11] in this paper, we report the synthesis of such dihydropyrenes substituted with oligothiophenes, and in the accompanying paper their photochemical and electrochemical properties.



1 2

Results and Discussion

To maximize the change in conjugation between the closed and open forms of the dihydropyrene switch, the conductive chain should be on opposite sides of the dihydropyrene, as shown in Figure 1. In the dihydropyrene (DHP) form, all π-orbitals can align; however, because of the step in the cyclophanediene (CPD) form, there is not good through alignment of π-orbitals from one side to the other (green-red-black in Figure 1). Thus the CPD form should be less conductive than the DHP form. When substituents are on the same side, as in **3**, the alignment of orbitals will also depend upon steric interactions between the substituents, and so it is not so obvious as to which form is more conducive to conductivity. From a synthesis point of view, the 4,5,9,10-positions of **2** are reactive to electrophilic substitution, so synthesis of the molecules in Figure 1 should not be a problem. However, as mentioned above, the parent **2** has a poor opening efficiency,[7] while that of the benzoswitch **4** is much better, and so we decided to start syntheses with **4**.



3 2 4

For **4**, only the 4,5-positions are active, and so substituents in the 10,11-positions would need to be pre-installed.

Synthesis of 4,5-Derivatives of 4. Our original synthesis[6] of **1** used 4,9-diiodo-**2** in a Suzuki coupling with thiopheneboronic acid; however, unfortunately, it is not possible to iodinate **4** (loss of the internal methyl groups occurs), and so the more sluggish bromo derivatives have to be used in couplings. Our original bromination of **4** with NBS in DMF/DCM was carried out <0 °C and gave ~50% of 4,5-dibromide **5**.[11b] Since then, we have found that better yields (80%) can be achieved at 25 °C, with fewer purification problems. In principle, coupling of dibromide **5** to an appropriate thiophene could be achieved using Suzuki, Kumada, or Stille conditions; however, because of the electron-rich DHP ring, all are very sluggish. With commercially available 2-thiopheneboronic acid, using Na_2CO_3 as base and $Pd(PPh_3)_4$ as catalyst, dibromide **5** gave 60−90% of bisthienyl-DHP **6** but required 48 h reaction time (Scheme 1). When bi- or terthienyl derivatives were used, the Stille coupling was found preferable to identify the extent of the conversions. Thus, 3 days at reflux was required to convert (60%) **5** into **7** using stannyl terthiophene **8**[12] with $Pd_2(dba)_3$, dppf catalysts. Product **7** was obtained as a rusty brown powder, with the internal methyl protons at δ −0.87, somewhat deshielded from those of **4**, δ −1.22. To lengthen the thiophene chains, **7** was reacted with *n*-BuLi to make the dianion and then with Bu_3SnCl to generate **9**, which on Stille coupling (as above) with dibromide **10** yielded 60% of **11**, with internal methyl protons at δ −0.86. As an alternative, the stannyl-quinquethiophene **12**, prepared[12] from **13**[13] on

(8) Choi, H.; Lee, H.; Kang, Y.; Kim, E.; Kang, S. O.; Ko, J. *J. Org. Chem.* **2005**, *70*, 8291–8297.

(9) (a) Dulic, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. *Phys. Rev. Lett.* **2003**, *91*, 207402-1-207402-4; (b) Katsonis, T.; Kudernac, T.; Walko, M.; van der Molen, S. J.; van Wees, B. J.; Feringa, B. L. *Adv. Mater.* **2006**, *18*, 1397–1400. (c) Xu, B.; Tao, N. J. *Science* **2003**, *301*, 1221–1223. (d) He, J.; Chen, F.; Liddell, P., A; Andreasson, J.; Straight, S. D.; Gust, D.; Moore, T. A.; Moore, A. L.; Li, J.; Sankey, O. F.; Lindsay, S. M. *Nanotechnology* **2005**, *16*, 695–702.

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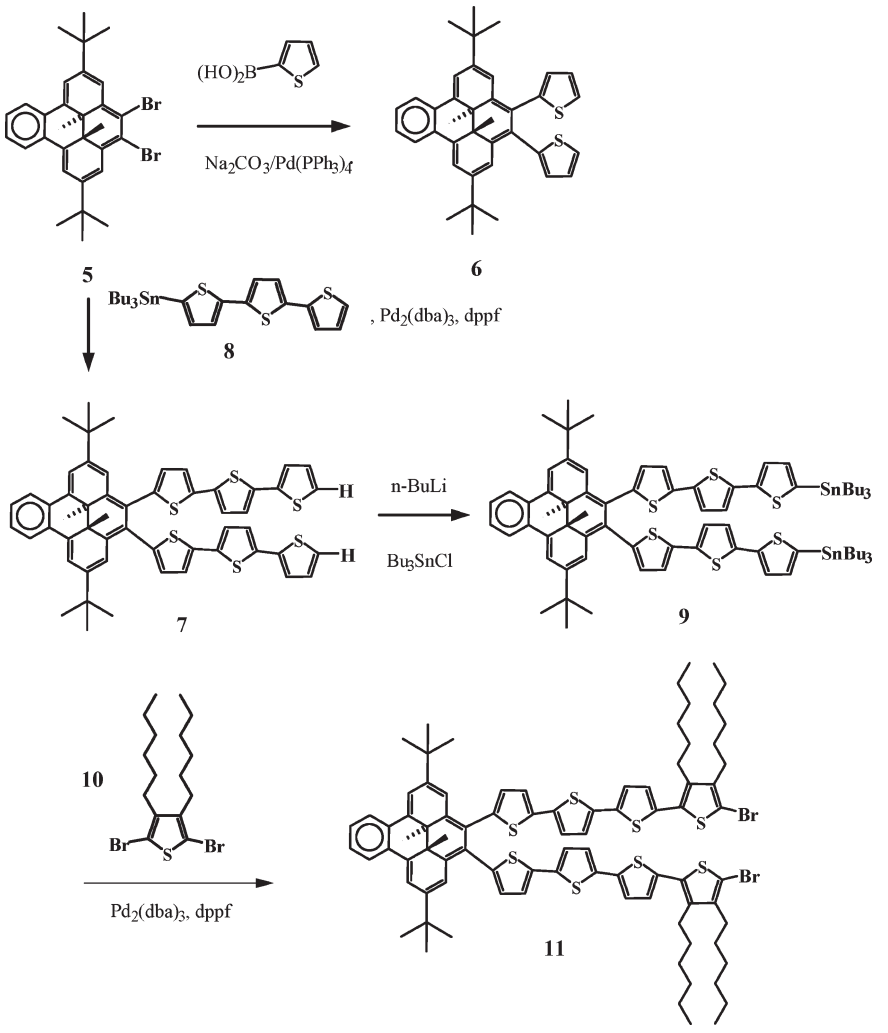
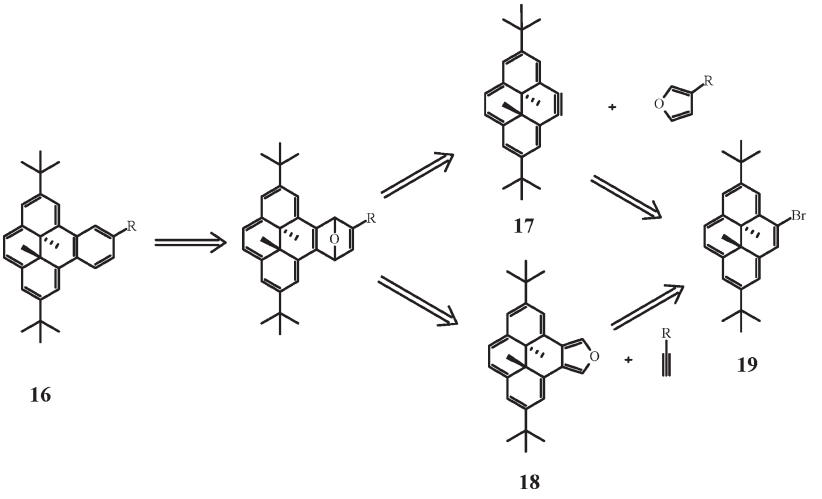
SCHEME 1. Typical Syntheses of Thienyl Dihydropyrenes

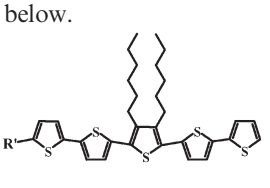


SCHEME 2. Retrosynthesis of 10-Substituted Benzo-dihydropyrenes

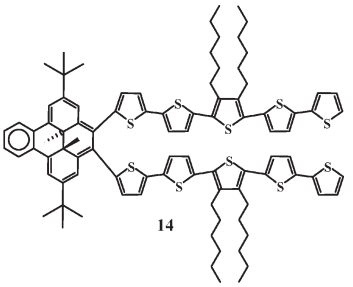


coupling for 4 days with **5** gave 20% of bis(pentathienyl)-DHP **14**. It was not just the fact that there were two bromines present in **5** that made couplings sluggish, even 4-bromo-**4**[11a] on reaction with **8** required 3 days to produce about 50% of terthienyl derivative **15**. As anticipated, all of these benzo-dihydropyrene derivatives (**6**, **7**, **11**, **14**, **15**)

easily photo-opened with visible light. This is discussed below.



12 R' = $SnBu_3$
13 R' = H



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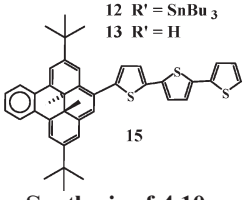
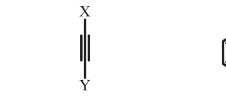
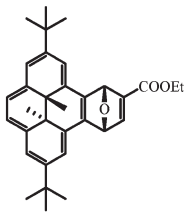


15

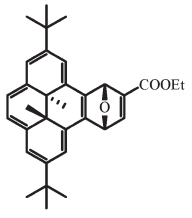
Synthesis of 4,10- or 4,11-Derivatives of 4. A logical retrosynthesis (Scheme 2) of 10-substituted benzo-dihydropyrenes (**16**) proceeds through a Diels−Alder reaction of either aryne **17** with an appropriately substituted furan[14] or furan **18** with an appropriately substituted acetylene. Both of **17** and **18** are derived from the bromide **19**.[15] The obvious substituent R in **16** is a bromine since that would enable easy coupling to thiophenes as described above. However, reaction of 3-bromofuran with aryne **17** gave a large number of non-useful products. The alternate approach through **18** with trimethylsilylethyne was equally unsuccessful, giving only a variety of dihydropyrene products derived from **18**. However, reaction of furan **18** with ethyl propiolate (**20a**) in refluxing toluene gave 71% yield of the adducts **21a**,**b**. Isomer **21b** was poorly soluble in hexanes, and so could be separated from **21a** for characterization purposes. The isomers could be assigned by careful comparison (see Experimental Section) with adduct **22**, obtained from diethyl acetylene dicarboxylate (**20b**) (74% yield, from refluxing toluene). The Weinreb amide[16] **20c** likewise gave two isomers of **23** in 66% yield.



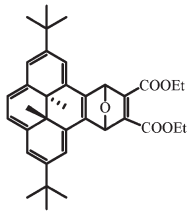
20a X=COOEt, Y=H
20b X=Y=COOEt
20c X=CON(Me)OMe



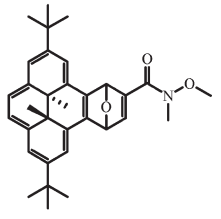
21a



21b

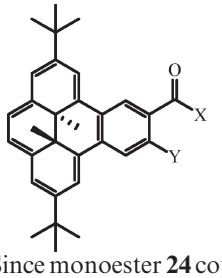


22



23a,b

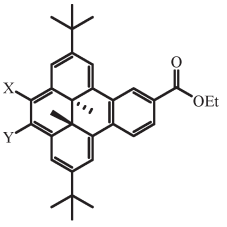
In principle, deoxygenation of **21**−**23** should give substituted benzodihydropyrenes (**16**), where the substituent(s) can then be used to couple to thiophene nuclei. Typically, we have used $Fe_2(CO)_9$ in refluxing benzene as a mild deoxygenating agent.[11b] With adduct **21**, a 72% yield of benzo-DHP **24** was obtained, *providing* only a small (10%) excess of iron carbonyl was used; otherwise, increased formation of green iron adducts was formed.[17] Adduct **22** similarly gave 80% of diester DHP **25**, but the Weinreb amide adducts **23** failed to deoxygenate properly to **26**.



24 X=OEt; Y=H
25 X=OEt; Y=COOEt
26 X=N(Me)OMe; Y=H
27 X=OH; Y=H
28 X=Cl; Y=H
29 X=2-thienyl; Y=H

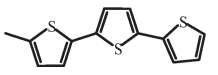
Since monoester **24** could easily be hydrolyzed with NaOH to acid **27**,[18] conversion of this to the acid chloride **28** or Weinreb amide **26** potentially could lead to the carbonyl coupled thiophene **29**.

We did not think having a carbonyl group as the coupling link would be a bad thing, as carbonyl groups appear to enhance dihydropyrene photochromicity.[11c] The effect of such a carbonyl on the electronic coupling of the DHP to the thiophene would need to be determined. However, before this was affected, introduction of thienyl groups onto the DHP side needs to be considered. Bromination of dihydropyrenes is fast, as is that of thiophenes, so selective bromination of the DHP nucleus in **29** might be quite difficult. We thus decided that it would be prudent to introduce the desired bromine before connecting to a thiophene. Thus, bromination of ester **24** with NBS in refluxing dichloromethane gave 91% of monobrominated product but as a 1:3 mixture of the 4-bromide **30a** and the 5-bromide **30b**, which unfortunately could not be separated. However, the large ratio of isomer amounts made assignment by their ^1H NMR peaks easy; for example, in C_6D_6, H-9 appears at δ 9.90 in **30b** and δ 9.88 in **30a**; the *t*-butyl protons are at δ 1.41 and 1.30 in **30a** but at δ 1.35 and 1.36 in **30b**. This isomer problem could be avoided by use of excess NBS to yield the dibromide **31**.

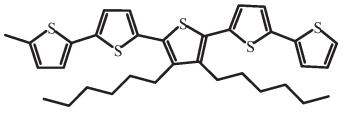


30a X=H; Y=Br
30b X=Br; Y=H
31 X=Y=Br
32a X=H, Y=R
32b X=R, Y=H
33a X=H, Y=R'
33b X=R', Y=H
34 X=Y=R

R=



R'=



which was coupled with stannyl terthiophene **8** in THF using $Pd_2(dba)_3$ and dppf catalysis at reflux for 80 h to yield 67% of

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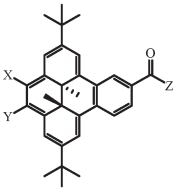
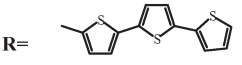
(17) Zhang, R.; Fan, W.; Twamley, B.; Berg, D. J.; Mitchell, R. H. *Organometallics* **2007**, *26*, 1888–1894.
(18) Lee, H-W; Robinson, S. G.; Bandyopadhyay, S.; Mitchell, R. H.; Sen, D. *J. Mol. Biol*. **2007**, *371*, 1163–1173.

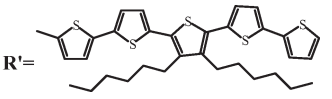
the bis-terthiophene product **34**, as a single isomer, which could thus be completely characterized, including the assignment of all protons and carbons in the NMR spectra. With this in hand, reaction of the mixed isomers of **30** with stannyl terthiophene **8** and pentathiophene **12** gave 77 and 56%, respectively, of the mixed isomers of **32** and **33**. Most proton and carbon signals could be assigned, and the mixtures gave correct HRMS *m*/*z* values and elemental analyses.

With the thiophene units installed on the DHP side of the molecule, installation on the benzo side could now begin. Hydrolysis of the esters **32** and **33** with aqueous ethanolic NaOH gave the corresponding acids **35** and **36**, which on reaction with *N*,*O*-dimethylhydroxylamine hydrochloride using DIC as coupling agent and a small amount of 4-(dimethylamino)pyridine (to avoid anhydride formation) gave overall yields from the esters of 71 and 75% of the Weinreb amides **37** and **38**. The new *O*-methyl and *N*-methyl signals of the amides were easily seen at δ 3.18 and 3.13 (major isomers, with minor isomers about 0.003 ppm different). Again correct HRMS *m*/*z* values and elemental analyses were obtained.



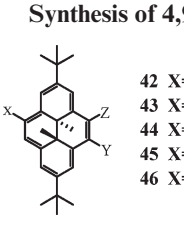
35a X=H, Y=R; Z=OH
35b X=R, Y=H; Z=OH
36a X=H, Y=R'; Z=OH
36b X=R', Y=H; Z=OH
37a X=H, Y=R; Z=N(Me)OMe
37b X=R, Y=H; Z=N(Me)OMe
38a X=H, Y=R'; Z=N(Me)OMe
38b X=R', Y=H; Z=N(Me)OMe
39a X=H, Y=R; Z=R
39b X=R, Y=H; Z=R
40a X=H, Y=R'; Z=R'
40b X=R', Y=H; Z=R'
41a X=H, Y=R; Z=R'
41b X=R, Y=H; Z=R'



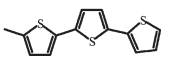


The Weinreb amides **37** and **38** were reacted with large excesses of the lithium derivatives of the terthiophene **8** (where R = Li) and pentathiophene **13** (where R′ = Li) at −78 °C to give 60% yields of the final products **39**−**41**. The excess of monolithio derivatives reduced disproportionation and formation of bislithio derivative products. In the products **39**−**41**, the amide OMe and NMe signals in the ^{1}H NMR spectra had disappeared and new thiophene signals were observed. Correct molecular ions were obtained in their mass spectra, as well as correct elemental analyses.

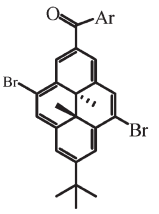
Synthesis of 4,9-Derivatives of Parent Dihydropyrene 2.



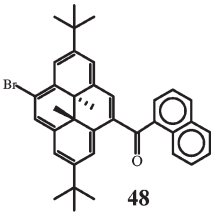
42 X=Y=H; Z= 1-naphthoyl
43 X=Br, Y=H; Z= 1-naphthoyl
44 X=Y=Br; Z= 1-naphthoyl
45 X=Y=R; Z= 1-naphthoyl
46 X=Y=Br; Z=H



During the course of this research, we discovered that introduction of an aroyl group onto the dihydropyrene nucleus (e.g., as in **42**) substantially improved the quantum yield of the photo-opening reaction of the DHP to the CPD (see Figure 1).[11c] This improved photochromicity inspired us to return to and pursue our originally perceived molecules of the type shown in Figure 1. Thus, bromination of **42** with NBS in DCM/DMF at room temperature *first* selectively introduces a bromine at the 10-position to yield 75% of monobromide **43**. Use of 2 equiv of NBS only forms about 40% of the dibromide **44**, along with a similar amount of **43**. It was anticipated that the electron-withdrawing carbonyl group would speed up the Stille reaction, and indeed, reaction of dibromide **44** with excess of the stannyl terthiophene **8** under similar conditions as above gave a 69% yield of the bis-terthiophene product **45** in only 18 h. Startlingly, however, *no trace* of photo-opening to the CPD form was observed when **45** was irradiated with visible light!!! We surmised that the thiophene chains were preventing co-planarity of the carbonyl function with the DHP ring, and so enhanced photochromicity was not observed. Fortunately, however, we also decided to synthesize dibromide **44** by naphthoylating the parent dibromide **46**. Much to our surprise, the expected product **44** was only obtained in 10% yield, but excitingly, 30% of the ipso-de-*tert*-butylated



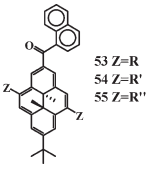
47 Ar = 1-naphthyl
49 Ar = 1-pyrenyl
50 Ar = benzoyl
51 Ar = 9-anthranyl



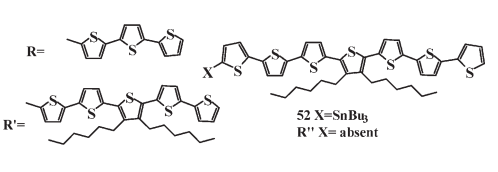
48

product **47** was obtained,[19] where the naphthoyl group had replaced one *t*-butyl group and so was now spacially separated from the bromo group, and as well in a much more effective position to enhance photochromicity.[11c] Indeed, **47** rapidly bleached, forming the CPD (see below) on exposure to visible light. This rather interesting Friedel−Crafts reaction also yielded 21% of the ipso-debrominated product **48**. To test its generality, 1-pyrenoyl chloride was used and gave 34% of analogous product **49**, while benzoyl chloride only gave 5% of **50** and 9-anthranoyl chloride only gave 13% of **51** under similar conditions. Evidently, as might be expected, the bulk of the aroylating agent affects the yield.

Stille coupling under similar conditions used above of the naphthoyl dibromide **47** with the stannyl terthiophene **8**, the pentathiophene **12**, and the septithiophene **52** gave, respectively, 91, 56, and 34% of the products **53**, **54**, and **55**.



53 Z=R
54 Z=R'
55 Z=R''

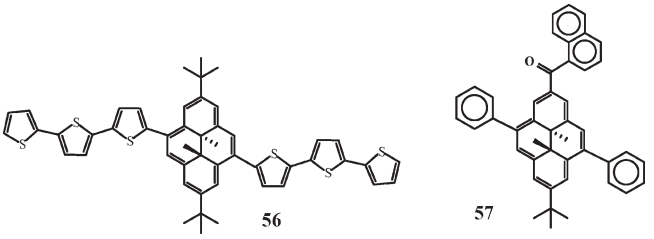


52 X=SnBu$_3$
R'' X= absent

In all three compounds, the carbonyl peaks could be seen at about δ 199 in the ^{13}C NMR spectra, and their IR stretches at ~1640 cm^{-1} in the IR spectra. In their ^{1}H NMR spectra,

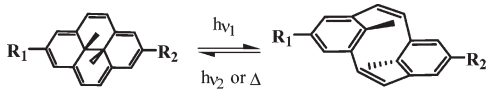
(19) Ayub, K.; Zhang, R.; Robinson, S. G.; Twamley, B.; Williams, R. V.; Mitchell, R. H. *J. Org. Chem.* **2008**, *73*, 451–456.

the internal methyl protons appeared as two singlets at δ −3.3 and −3.4. Importantly, all three compounds opened very quickly on irradiation with visible light to form the CPD forms (see below). For photo-opening comparison studies, the dibromide **46** was also Stille coupled with **8** to give 68% of **56** and the naphthoyl dibromide **47** was coupled with phenylboronic acid to give (quantitatively) **57**.



56 **57**

Photochemical Opening of the DHPs to the CPDs.



2	**R_1, R_2 = t-Bu**	**2'**
58	**R_1, R_2 = H**	**58'**
DHP		**CPD**

Dihydropyrenes such as **58** are classified as negative-T photochromes[20] because the "closed" colored DHP isomer **58** is thermally stable and, on irradiation with longer wavelength light, forms the colorless "open" CPD form **58′**, which can be transformed back to DHP **58** either with shorter wavelength light or thermally. The parent **58** is actually not a very good photochrome because the quantum yield of ring opening to give **58′** is only 0.006,[7] and in fact, with *t*-butyl groups present as in **2**, it is even worse, 0.0015. Fortunately, introduction of electron-withdrawing groups such as carbonyl or nitro groups, or fusion of a benzene ring as in **4**, substantially increases the photo-opening quantum yield[7,11c] and hence make these systems more usable. All of the DHPs synthesized above were tested for ease of photo-opening to the CPD form [Note: the open CPD form always has the same number as the closed DHP form, with an additional prime (′) attached, e.g., DHP **2** has CPD form **2′**]. Benzo-DHPs **6**, **7**, **14**, **15**, **24**, **25**, **32**, **33**, **34**, **39**, **40**, and **41** and naphthoyl-DHPs **53**, **54**, and **55** all opened easily upon irradiation with visible light of wavelength >490 nm. Since the quantum yields of the CPD to DHP closing reaction are all high (∼0.4), it is necessary during the photo-opening reaction to avoid irradiating into the tail of the CPD form. So if the CPD has a conjugated system attached which extends its absorption tail, light further to the red is required. For example, for benzo-DHP **4**, white light from a tungsten bulb can be used; for the oligothiophene compounds used here, white (tungsten) light with a 490 nm cutoff filter was satisfactory. Interestingly, the only compounds that failed to open when irradiated with >490 nm light were **45** and **56**. In DHP **45**, the naphthoyl substituent is *ortho* to the terthienyl substituent, and since the 4-naphthoyl-DHP **42** opens relatively easily,[11c] it is suggestive that co-planarity of the carbonyl with the π-system is desirable, and the bulky thienyl groups are preventing this. Robb[21] has shown that the photo-opening reaction for **58** occurs through a conical intersection between a biradical excited state and the ground state. This is inefficient because the biradical excited state is not the lowest excited state minimum and so is not highly populated, and there are no pathways from the more populated zwitterionic excited state. π-Acceptor groups, such as naphthoyl, stabilize radicals and may change the energies of the states and their relative populations. Certainly, experimentally, addition of naphthoyl (or equivalent) groups dramatically improves the photo-opening reaction,[11c] and we were expecting them to do so here, especially for **53**−**55**, where no steric effects can come into play. For the bisterthienyl-DHP **56**, no activating group is present, and no photo-opening was observed even after several hours irradiation.

Quantum yield comparisons are the "gold standard" for photochemical reactions; however, we have found[22] that comparison of the side-by-side relative opening rates with a standard (e.g., benzo-DHP **4**) is much faster to carry out and is just as useful since we are really interested in "just how fast does the photochrome open under the same 'practical conditions' as one of our standards". Practical conditions in reality often means "with the same lamp" and not necessarily with monochromatic radiation, as is used for quantum yield determinations.

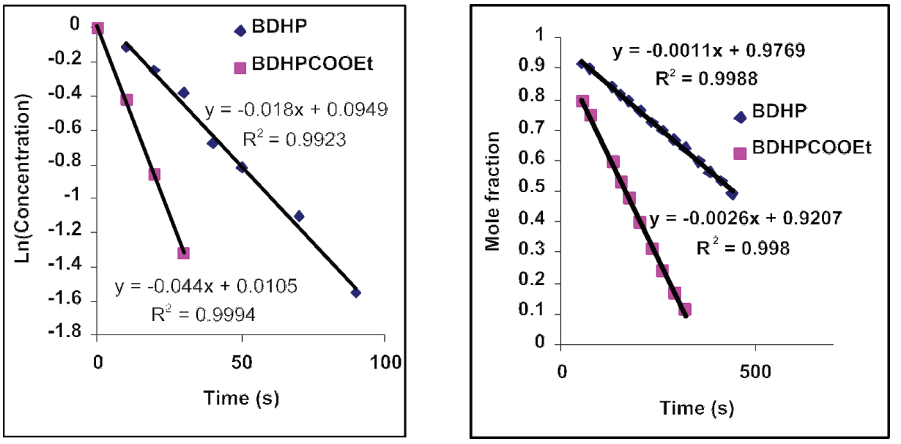
In principle, the photo-opening of a DHP to a CPD can be followed using visible absorption data to estimate concentration or by using ^{1}H NMR integrals. In either case, a reference sample is used, here benzo-DHP **4**. For a simple photochemical reaction of molecule A interacting with light, then typically a second-order rate law is applied such that rate = k[A][light]. However, since to an approximation [light] is constant, this becomes a pseudo-first-order reaction, where the apparent rate constant, k', can be obtained from the slope of a graph of ln[A] versus time. Use of UV−visible spectroscopy to monitor the rate of the photochemical reaction thus yields the apparent rate constant k'. When NMR is used to estimate changes in concentration, much more concentrated solutions are used than for UV−vis determinations, and then light only penetrates the outer perimeter of the NMR tube, bleaching only those molecules, and then can pass to the next layer bleaching those, and so on. Essentially, the number of molecules being irradiated at any one time is virtually a constant, and so under NMR conditions, the rate equation becomes a pseudo-zero-order reation, where the apparent rate constant, k'', can be obtained from a plot of [A] versus time. In the actual experiments, the sample and the reference are irradiated side by side at the same time. Figure 2 shows the results for both experiments for the benzo-DHP ester **24** (BDHPCOOEt) in comparison to benzo-DHP **4** (BDHP).

For **24** (or **4**), the apparent rate constants k' and k'' are of course not the same, *but* the ratio of rate constants, $k'_{\mathbf{24}}/k'_{\mathbf{4}}$ and $k''_{\mathbf{24}}/k''_{\mathbf{4}}$ are the same, 2.4! Thus, under the same conditions, the ester **24** photo-opens approximately 2.4 times faster than the parent **4**.

(20) Bouas-Laurent, H.; Durr, H. *Pure Appl. Chem.* **2001**, *73*, 639–665.

(21) Boggio-Pasqua, M.; Bearpark, M. J.; Robb, M. A. *J. Org. Chem.* **2007**, *72*, 4497–4503.

(22) (a) Mitchell, R. H.; Brkic, Z.; Sauro, V. A.; Berg, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 7581–7585. (b) Mitchell, R. H.; Fan, W.; Lau, D. Y. K.; Berg, D. J. *J. Org. Chem.* **2004**, *69*, 549–554.

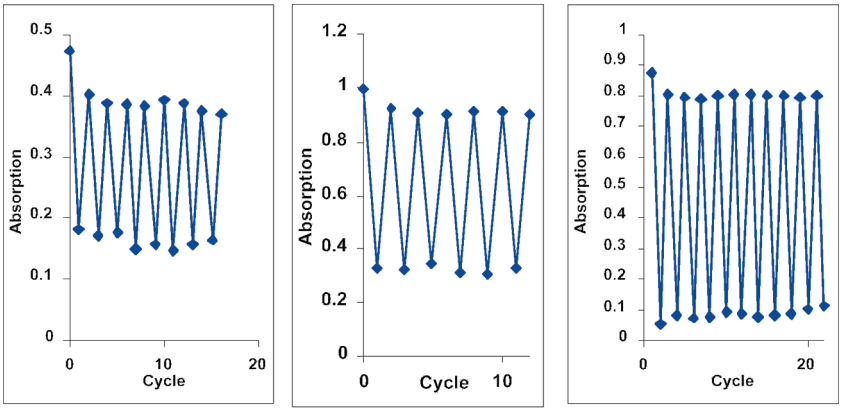


(a) UV-vis: (b) ^{1}H NMR

$k'_{24}/k'_4 = 0.044/0.018$ $k''_{24}/k''_4 = 0.0026/0.0011$

$= 2.44$ $= 2.36$

FIGURE 2. Comparison of the photo-opening rates of the benzo-DHP ester **24** and the benzo-DHP **4**, carried out side by side at the same time, (a) in cyclohexane using UV−vis to monitor the reaction, and (b) in C_6D_6 using ^{1}H NMR spectroscopy to monitor the reaction.



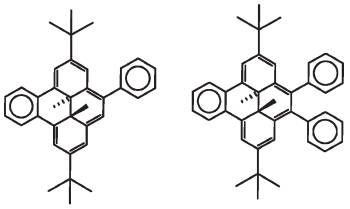
14 (554nm) **40** (550 nm) **54** (566nm)

FIGURE 3. Cycling visible light opening (> 490 nm filter) and UV (254 nm) closing in cyclohexane while monitoring the ~550 nm absorption of the DHP for compounds **14**, **40**, and **54**.

Table 1 then shows the relative rates of photo-opening for selected compounds. Two observations quickly become apparent: first, as one goes from thienyl to terthienyl to pentathienyl substituents on a benzo-DHP (compare **4**−**6**−**7**−**14** or **24**−**39**−**40**), the rate of photo-opening dramatically increases. Second, addition of a naphthoyl group at the 2-position of a DHP dramatically increases its rate, which is further amplified by additional thienyl or phenyl substituents (compare **47**−**56**−**53**−**54**). One phenyl substituent appears to be more effective than one 2-thienyl, but not as good as terthienyl (compare **59**−**60**−**6**−**7**). Compound **54** is probably the fastest opening DHP photochrome known at this time, and although we do not have a quantum yield available yet, in comparison to other more recently obtained systems, we estimate it will be around 0.4, which makes this system competitive with other photochromes.

UV Closing and Cycling. Generally, the quantum yields of closing from CPD to DHP are high, ~0.4 for most CPDs studied,[7] and when relative rate studies versus benzo-CPD **4′** are carried out, as above, no significant variation is found. For example, compounds **14** and **40** both closed at the same rate as benzo-CPD **4′**. The CPD **54′** derived from the fastest opening DHP **54**, however, did close back approximately twice as fast as benzo-CPD **4′**. These three compounds, **14**, **40**, and **54**, contain the longest pentathienyl units, and both the DHP and CPD forms have extensive absorption in the visible region. It was thus important to show that these cycle between open and closed forms (Figure 3). Note that irradiation started from pure DHP (high absorption) to CPD (low absorption) to DHP etc. For the fastest opening **54**, the DHP and CPD absorption spectra are shown in Figure 4.

TABLE 1. Relative Photo-opening Rates of Selected Compounds Compared to Benzo-DHP 4 (BDHP) Determined in Cyclohexane Using UV−Visible Spectroscopy (in Increasing Order; Np = Naphthyl; Th_3 = terthienyl; Th_5 = pentathienyl)



59 60

Compound	Relative rate to 4
4 (BDHP)	1.0
24 (EtOOC-BDHP)	2.4
6 (BDHP-$(Th)_2$)	2.5[a]
59 (BDHP-Ph)	4.2[b]
47 (NpCO-DHP-Br_2)	7.4
60 (BDHP-Ph_2)	8[c]
7 (BDHP-$(Th_3)_2$)	12
14 (BDHP-$(Th_5)_2$)	20
39 (Th_3CO-BDHP-Th_3)	20
56 (NpCO-DHP-Ph_2)	24
40 (Th_5CO-BDHP-Th_5)	30
53 (NpCO-DHP-$(Th_3)_2$)	50
54 (NpCO-DHP-$(Th_5)_2$)	130

[a]Determined by NMR in toluene. [b]From ref 23. [c]From ref 24. Estimated relative rate (error): 2 (±0.2); 10 (±0.5); 20 (±1); 50 (±2); 130 (±5). The rate data (of the form shown in Figure 2) are presented in the Supporting Information.

The spectra in Figure 4 were obtained by irradiation of the film with visible light from a tungsten bulb with a >490 nm cutoff filter. Essentially, the same result was obtained if a red laser pointer (650 nm, <5 mW) was used. However, if a green laser pointer (532 nm, <5 mW) was used, a photostationary state was observed, where presumably irradiation into both forms occurs. The spectra are shown in Figure S1 in the Supporting Information.

Extended irradiation of DHP **54** with 254 nm (but not 350 nm) light caused some decomposition; in cyclohexane-d_{12}, no new NMR peaks were observed, but after 40 h, it was observed that a film formed on the inside of the NMR tube, suggesting polymerization is occurring. When a thin film of **54** was irradiated for 3 h with 254 nm light, and then dissolved in $CDCl_3$, and a ^{1}H NMR spectrum then obtained, the peaks for the DHP protons H-5,8,10 and thiophene protons H-27,47,48 were broadened (Figure 5) but returned to normal after filtration through a small plug of alumina, suggestive that some sort of reactive intermediate was present, which strongly enhances the thermal closing of the CPD

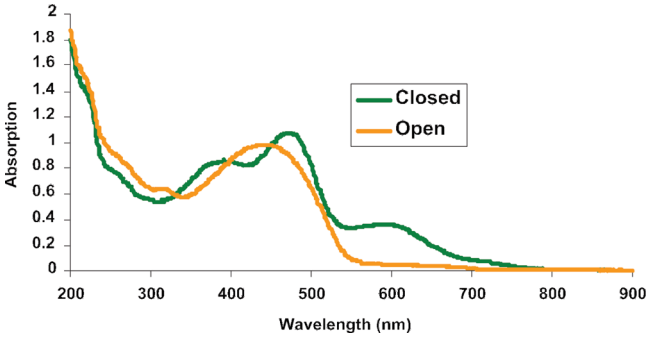


FIGURE 4. Absorption spectra of a thin film cast from dichloromethane of the most conjugated species, compound **54** (closed, DHP) and **54′** (open, CPD).

form **54′**. If this film solution was opened with visible light to CPD **54′**, thermal closing took only 3 min at 22 °C, whereas if non-irradiated film was used, thermal closing took 140 min (see Supporting Information Figure S2). Since the DFT calculations of Williams[19,25] suggest that the transition state for the thermal closing reaction has biradical character, it is not difficult to anticipate that any preformed DHP radicals might easily enhance the observed rate, and thus the intermediate may have radical character, which is removed on filtration through alumina, and thus restores the normal thermal rate. Broadening of DHP peaks by the presence of biradicals has been observed before.[26]

Thermal Closing Reactions of CPDs to DHPs. Understanding the thermal electrocyclization of CPDs to DHPs, which are Woodward−Hoffmann forbidden reactions, has proved to be more difficult than one might imagine.[19,25] Energies of activation (E_{act}) tend to be somewhat misleading for this reaction since there appears to be a large variation in pre-exponential factor from system to system.[19] We have thus found that comparison of thermal conversion half-lives ($\tau_{1/2}$) at two temperatures, 20 and 50 °C, tends to give more useful results. Here, we studied the thermal closing reactions using ^{1}H NMR spectroscopy integrations to obtain rate data for the CPD to DHP thermal reaction. Table 2 gives the $\tau_{1/2}$ values at 20 and 50 °C for the systems studied, while full E_{act}, ln A, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ data (derived from Arrhenius and Eyring plots) are given in the Supporting Information.

Consistent with Williams calculations,[25] introduction of the radical stabilizing carbonyl containing naphthoyl group at the 2-position of the DHP (the site of highest peripheral spin density in the transition state) increases the speed of the thermal return most (compare **2′** and **44′**). This is further increased by addition of phenyl and thienyl groups (**53′**, **54′**, **57′**). Interestingly, introduction of the carbonyl group onto the benzo ring of benzo-DHP **4** as in **39′** and **40′** only has a small effect, presumably positions of lower spin density. Addition of two sets of thienyl groups to the DHP side of BDHP **4** as in **6′**, **7′**, and **14′**, however, does give a substantial rate increase, with the shorter thiophene units appearing to have the greatest effect.

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(24) Bandyopadhyay, S. Ph. D. Thesis, University of Victoria, **2004**.

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

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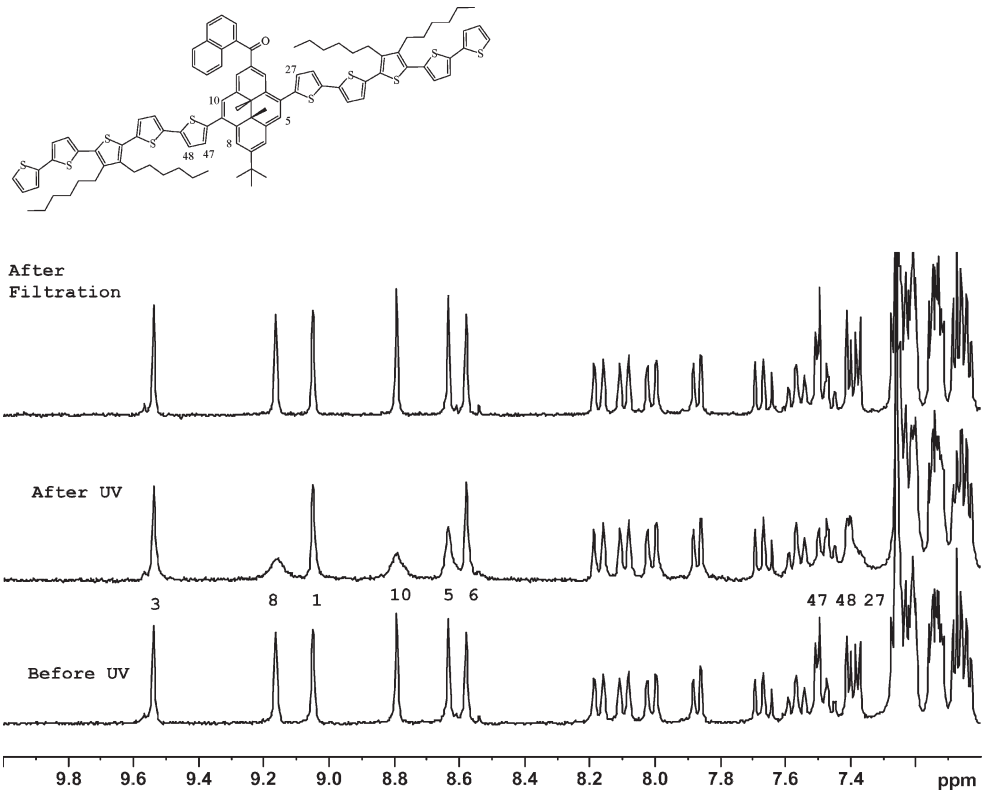

FIGURE 5. Part of the ^{1}H NMR spectra of **54** before and after 254 nm and then after filtration through alumina. Note broadening of signals for H-5,8,10,27,47,48.

TABLE 2. Half-Lives ($\tau_{1/2}$) at 20 and 50 °C for the Thermal Closing Reaction of Selected CPDs into DHPs in Either $CDCl_3$ (*) or C_6D_6 (#) Estimated from ^{1}H NMR Derived Rate Data, Arranged by DHP and BDHP in Increasing Order of $\tau_{1/2}$ (20 °C) (Estimated Errors in $\tau_{1/2}$ are ±5%)

Compound	$\tau_{1/2}$ (20 °C)	$\tau_{1/2}$ (50 °C)
53′ (NpCO-DHP-$(Th_3)_2$	(*) 41 min	1.1 min
54′ (NpCO-DHP-$(Th_5)_2$	(*) 57 min	2.5 min
57′ (NpCO-DHP-$(Ph)_2$	(*) 94 min	2.6 min
44′ (NpCO-DHP-$(Br)_2$[19]	(*) 3.4 h	5.7 min
2′ (DHP)[19]	(*) 54 h	2.0 h
6′ BDHP-$(Th)_2$	45 h[a,b]	1.1 h
7' (BDHP-$(Th_3)_2$	(#) 59 h	1.1 h
14' (BDHP-$(Th_5)_2$	(#) 69 h	1.2 h
40' (Th_5CO-BDHP-Th_5)	(#) 4.5 days	2.5 h
39' (Th_3CO-BDHP-Th_3)	(#) 6.6 days	3.2 h
4' (BDHP)[11b,19]	7.3 days[a]	5.2 h
24' (EtOOC-BDHP)	(#) 8.8 days	3.8 h

[a]Measured in toluene. [b]UV determination.

In terms of compromise between photochromicity and thermal closing, the thienyl-BDHPs **39** and **40** show much improved photo-opening rates (20−30 times BDHP **4**) but also reasonably good thermal stability of the corresponding CPDs **39′** and **40′**, not much changed from BDHP **4**, and so depending upon the intended application, look to be reasonable switches. The naphthoyl-DHP derivatives, **53** and **54**, while showing excellent photo-opening properties, have poorer thermal stability of the corresponding CPDs, and would be good switches where a short "open" time is required.

Conclusions

In this paper, the synthesis and photochemical properties of several different length oligothiophenes with either a photochromic DHP or BDHP switch inserted into the thiophene chain are reported. When a 2-naphthoyl-DHP is the inserted switch (e.g., **53** or **54**), very fast photo-opening of the DHP to CPD can be obtained, suggesting that a good quantum yield will be obtained, but relatively fast thermal closing ($\tau_{1/2} \sim 1$ h at 20 °C) is also observed, limiting some applications. When BDHPs are inserted such that the thiophenes are both connected to the DHP side of the BDHP, slower thermal closing rates are observed (e.g., $\tau_{1/2} \sim 3$ days at 20 °C for **7′** and **14′**), which are only about twice that of BDHP itself, but with reasonably good improvement of the photo-opening reaction 10−20 times that of BDHP itself. When the BDHPs are inserted such that one oligothiophene is attached to the DHP side of BDHP and the other oligothiophene is attached through a carbonyl group to the benzo side of the BDHP, then excellent improvement in photo-opening rate (20−30 times that of BDHP) coupled with good thermal stability ($\tau_{1/2} \sim 5-7$ days, not much changed from BDHP itself) is obtained. In our opinion, these now make DHPs quite good photochromes and certainly competitive with other systems.

The accompanying paper focuses on the electrochemical and conductive properties of a selection of the above compounds, together with a discussion of the conjugation changes taking place on switching.

Experimental Section

The syntheses of **5**, **6**, **9**, **11**, **15**, **22**, **23**, **25**, **31**, **33**, **34**, **35**, **36**, **37**, **38**, **41**, **43**, **44**, **45**, **48**, **49**, **50**, **51**, **55**, **56** and CPDs **15′**, **25′**, **30′**, **31′**, 32′, **33′**, **34′**, **36′**, **38′**, **39′**, **41′**, and **55′** and the general conditions and the numbering system used for NMR assignments are

given in the Supporting Information. Note: $Pd_2(dba)_3$ = bis-(dibenzylideneacetone)palladium(0); dppf = bis(diphenylphosphino)ferrocene.

2,7-Di-*tert*-butyl-12c,12d-dimethyl-4,5-di-(2−5,2′:5′,2″-terthienyl)-*trans*-12c,12d-dihydrobenzo[*e*]pyrene 7. $Pd_2(dba)_3$ (10 mg, 0.011 mmol) and dppf (14 mg, 0.025 mmol) were added to a solution of 2-tributylstannyl-5,2′:5′,2″-terthiophene **8**[12] (855 mg, 1.59 mmol) and the dibromide **5** (226 mg, 0.409 mmol) in dry THF (10 mL), and the solution was heated to reflux for 63 h. The reaction mixture was then cooled, and aqueous KF (5 mL) was added, and the reaction mixture stirred a further 15 min. It was filtered through Celite washing with hexanes. The solution was then washed with water (3 × 100 mL), dried over $MgSO_4$, filtered through Celite, and the solvent evaporated. The product was purified by chromatography on silica gel (deactivated with 5% H_2O) using hexanes until all the excess terthiophene had been eluted and then 10:1 hexanes/dichloromethane to obtain 218 mg (60%) of the product **7** as a rusty brown powder, which on recrystallization from acetonitrile gave mp 167−169 °C: ^{1}H NMR (C_6D_6) δ 8.81−8.76 (*AA′*XX′, 2H, H-9,12), 8.44 (d, J = 1.2 Hz, 2H, H-1,8), 8.01 (d, J = 1.2 Hz, 2H, H-3,6), 7.55−7.51 (AA*XX*′, 2H, H-10,11), 6.98 (d, J = 3.5 Hz, 2H, H-15), 6.889 (d, J = 3.5 Hz, 2H, H-14), 6.887 (d, J = 3.6 Hz, 2H, H-24), 6.80 (d, J = 3.7 Hz, 2H, H-18), 6.73 (d, J = 3.7 Hz, 2H, H-19), 6.67 (dd, J = 1.2 Hz, 5.1 Hz, 2H, H-22), 6.60 (dd, J = 3.6, 5.1 Hz, 2H, H-23), 1.36 (s, 18H, 2,7-C(CH_3)$_3$), −0.87 (s, 6H, 12c,d-CH_3); ^{13}C NMR (C_6D_6) δ 147.1 (C-2,7), 141.2 (C-13), 138.6 (C-12b,12e), 138.5 (C-16), 137.9 (C-21), 137.2 (C-17), 136.8 (C-3a,5a), 136.6 (C-20), 130.6 (C-14), 130.3 (C-12a,12f), 128.4 (C-23), 127.2 (C-10,11), 126.9 (C-4,5), 125.5 (C-9,12), 125.1 (C-19), 124.8 (C-22), 124.7 (C-18), 124.3 (C-24), 124.0 (C-15), 119.4 (C-3,6), 118.1 (C-1,8), 37.2 (C-12c,12d), 36.2 (2,7-C(CH_3)$_3$), 30.9 (2,7-C(CH_3)$_3$), 18.9 (12c,d-CH_3); IR (film) ν 3065, 2962, 2923, 2865, 1475, 1446, 1368, 1258, 872, 836, 789, 755, 739, 692 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 250 (28 000), 355 (47 300), 507 (69 800), 510 (6630); LSIMS, m/z 886.1 (M+); HRMS calcd for $C_{54}H_{46}S_6$ 886.1924, found 886.1924. Anal. Calcd: C, 73.12; H, 5.23. Found: C, 72.27; H, 5.45.

2,7-Di-*tert*-butyl-4,5-di-(2−3″,4″-dihexyl-5,2′:5′,2″:5″,2‴:-5‴,2⁗-quinquethienyl)-12c,12d-dimethyl-*trans*-12c,12d-dihydrobenzo[*e*]pyrene 14. $Pd_2(dba)_3$ (35 mg, 0.038 mmol) and dppf (40 mg, 0.077 mmol) were added to a solution of the dibromide **10**[13a] (210 mg, 0.38 mmol) and 2-tributylstannyl-3″,4″-dihexyl-5,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene **12**[12,13] (750 mg, 0.86 mmol) in dry THF (8 mL) and then refluxed for 4 days. The solution was cooled; aqueous KF (10 mL) was added, and the reaction mixture stirred a further 15 min. It was then filtered through Celite using dichloromethane as eluant. The organic layer was washed, dried ($MgSO_4$), and filtered through Celite again. After solvent evaporation, the product was purified by chromatography on silica gel using first hexanes as eluant, followed by hexanes/dichloromethane (20:1) to elute the excess thiophene **13**, followed by hexanes/dichloromethane (10:1) to elute 120 mg (20%) of product **14** as a red solid, mp 98−100 °C: ^{1}H NMR (C_6D_6) δ 8.81−8.77 (AA′XX′, 2H, H-9,12), 8.45 (s, 2H, H-1,8), 8.04−8.01 (m, 2H, H-3,6), 7.55−7.51 (AA′XX′, 2H, H-10,11), 7.06−7.02 (m, 2H), 7.01−6.97 (m, 4H), 6.96−6.89 (m, 7H), 6.81−6.78 (m, 1H), 6.75−6.68 (m, 2H), 6.66−6.62 (m, 2H), 2.87−2.72 (m, 8H, H-39,45), 1.69−1.58 (m, 8H, H-40,46), 1.41−1.34 (m, 8H, H-41,47), 1.37 (s, 18H, H-13), 1.32−1.24 (m, 16H, H-42,43,48,49), 0.95−0.85 (m, 12H, H-44,50), −0.87 (s, 6H, H-15,16); ^{13}C NMR (C_6D_6) δ 147.13, 147.10, 141.34, 141.26, 141.23, 141.1, 140.9, 138.7, 138.6, 138.5, 138.38, 138.36, 138.0, 137.9, 137.8, 137.7, 137.4, 136.8, 136.3, 136.0, 135.5, 135.4, 131.11, 131.09, 130.9, 130.8, 130.7, 130.3, 128.92, 128.90, 128.4, 127.9, 127.5, 127.35, 127.2, 126.9, 125.5, 125.3, 125.23, 125.17, 125.13, 125.01, 124.95, 124.92, 124.91, 124.87, 124.8, 124.5, 124.43, 124.37, 124.05, 119.4 (C-3,6), 118.1, 37.2, 36.2, 32.17, 32.15, 31.4, 30.9, 30.3, 30.24, 29.0, 28.9, 23.35, 19.0, 14.7, 14.6; IR (film) ν 3065, 2954, 2925, 2856, 1464, 1367, 872, 789, 755, 690 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 251 (67 000), 346 (50 800), 412 (103 000), 554 (5380); LSIMS, m/z 1552 (M+), calcd for $C_{94}H_{102}S_{10}$ 1552.

10-Carboethoxy-2,7-di-*tert*-butyl-9,12-epoxy-*trans*-12c,12d-dimethyl-9,12,12c,12d-tetrahydrobenzo[*e*]pyrene 21. Ethyl propriolate (**20a**) (0.72 mL, 6.9 mmol) was added to a solution of the furan **18**[15] (273 mg, 0.710 mmol) in toluene (60 mL), and the reaction mixture was heated at 110 °C for 3 h. Over this time, the solution turned from a reddish purple to a light green. The reaction mixture was then cooled to room temperature and the solvent evaporated. The product mainly consists of two isomers of the product **21**, of which **21a** is much more soluble in hexane than isomer **21b**. The latter could be obtained reasonably pure by trituration with hexane as an insoluble green powder (128 mg, 36%). The hexane extract was purified by chromatography on silica gel (deactivated with 5% water) using hexanes/ethyl acetate (20:1) as eluant and gave a mixture of isomers **21a** and **21b** (120 mg, 35%) as a brownish powder. These could be combined with the previously obtained **21b** for direct use in the next step. For characterization purposes, recrystallization of the mixture from hexanes several times yielded the less soluble isomer **21b** as a green powder, mp 185−188 °C (color change at 109−112 °C). The more soluble isomer **21a** was isolated by recrystallization from hexanes of the collected mother liquors from the previous recrystallizations as green crystals, mp 185−186 °C.

Less Soluble Isomer 21b: ^{1}H NMR (C_6D_6) δ 8.53 (d, J = 1.2 Hz, 1H, H-8), 8.18 (br s, 2H, H-3,6), 8.07 (d, J = 0.8 Hz, 2H, H-4,5), 8.05 (d, J = 1.3 Hz, 1H, H-1), 7.39 (d, J = 1.9 Hz, 1H, H-11), 6.95 (d, J = 0.8 Hz, 1H, H-9), 6.33 (dd, J = 1.9, 0.8 Hz,1H, H-12), 3.97 (dq, J = 10.9, 7.1 Hz, 1H, OCH_2CH$_3$), 3.83 (dq, J = 10.9, 7.1 Hz, 1H, OCH_2CH$_3$), 1.58 (s, 9H, 2-C(CH_3)$_3$), 1.56 (s, 9H, 7-C(CH_3)$_3$), 0.84 (t, J = 7.1 Hz, 3H, −OCH$_2$CH_3), −2.72 (s, 2H, 12c-CH_3), −3.04 (s, 2H, 12d-CH_3); ^{13}C NMR (C_6D_6) δ 163.8 (C=O), 149.7 (C-11), 148.2 (C-10), 146.4 (C-2), 146.1 (C-7), 138.6 (C- 3a), 138.1 (C-5a), 135.8 (C-12f), 134.5 (C-12a), 129.8 (C-12e), 129.0 (C-12b), 125.7 (C-4/5), 125.5 (C-5/4), 122.5 (C-6), 122.2 (C-3), 116.9(C-8), 115.0 (C-1), 82.6 (C-12), 82.0 (C-9), 60.7 (OCH$_2$CH$_3$), 36.2 (2,7-C(CH_3)$_3$), 34.2 (C-12d), 33.5 (C-12c), 31.9 (2,7-C(CH_3)$_3$), 17.5 (12c-CH_3), 15.0 (12d-CH_3), 14.6 (OCH$_2$CH_3).

More Soluble Isomer 21a: ^{1}H NMR (C_6D_6) δ 8.53 (d, J = 1.3 Hz, 1H, H-8), 8.22 (d, J = 1.3 Hz, 1H, H-6), 8.19 (d, J = 1.2 Hz, 1H, H-3), 8.09 (s, 2H, H-4,5), 8.07 (d, J = 1.2 Hz, 1H, H-1), 7.60 (d, J = 2.0 Hz, 1H, H-11), 7.0 (dd, J = 0.9, 0.4 Hz, 1H, H-9), 6.30 (ddd, J = 2.0, 0.9, 0.4 Hz, 1H, H-12), 3.91 (dqd, J = 10.9, 7.1, 0.4 Hz, 1H, OCH_2CH$_3$), 3.78 (dqd, J = 10.9, 7.1, 0.4 Hz, 1H,OCH_2CH$_3$), 1.58 (s, 9H, 7-C(CH_3)$_3$), 1.57 (s, 9H, 2-C(CH_3)$_3$), 0.83 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), −2.79 (s, 3H, 12d-CH_3), −3.16 (s, 3H, 12c-CH_3); ^{13}C NMR (C_6D_6) δ 163.8 (C=O), 149.8 (C-11), 147.7 (C-10), 146.4 (C-2), 146.2 (C-7), 138.33 (C-5a), 138.28 (C-3a), 135.6 (C-12f), 134.6 (C-12a), 129.61 (C-12e), 129.56 (C-12b), 125.7 (C-5), 125.3 (C-4), 122.5 (C-6), 122.2 (C-3), 116.3 (C-8), 115.4 (C-1), 83.1 (C-9), 81.8 (C-12), 60.7 (OCH$_2$CH$_3$), 36.3 (2,7-C(CH_3)$_3$), 34.5 (C-12c), 33.0 (C-12d), 31.92 and 31.89 (2,7-C(CH_3)$_3$), 17.6 (12d-CH_3), 15.52 (12c-CH_3), 14.51 (OCH$_2$CH$_3$); UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 352 (41 900), 361 (41 300), 383 (35 800), 464 (11 400), 575 (285), 643 (605); IR (KBr) ν 1714, 1231, 1095, 876, 652 cm^{-1}; EIMS, m/z 482 (M$^+$); HRMS calcd for $C_{33}H_{38}O_3$ 482.2821, found 482.2807. Anal. Calcd: C, 82.12; H, 7.93. Found: C, 82.57; H, 7.91.

10-Carboethoxy-2,7-di-*tert*-butyl-12c,12d-dimethyl-*trans*-12c,12d-dihydrobenzo[*e*]pyrene 24. $Fe_2(CO)_9$ (106 mg, 0.292 mmol) was added to a solution of the furan adducts **21** (132 mg, 0.266 mmol) in degassed benzene (50 mL), and the solution was heated to reflux for 4 h during which time it turned from green to red. The solution was then filtered through a small (5 cm) silica gel column using

benzene as eluant, and then the solvent was evaporated. The product was purified by chromatography on silica gel (60−200 mesh, deactivated with 5% water) using hexanes/ethyl acetate (2:1) as eluant to give 89 mg (72%) of the product **24** as a red solid. This was followed by a small amount of a green iron adduct. On larger scales, an additional short alumina column using hexanes as eluant was needed to separate the product from the green iron adduct. Recrystallization from acetonitrile gave a red crystals, mp 140−141 °C: ^{1}H NMR (C_6D_6) δ 10.00 (s, 1H, H-9), 8.86 (d, J = 8.7 Hz, 1H, H-12), 8.67 (s, 1H, H-8), 8.53 (d, J = 1.1 Hz, 1H, H-11), 8.51 (s, 1H, H-1), 7.54 (s, 1H, H-3), 7.51 (s, 1H, H-6), 7.24 (AB, J = 6.5 Hz, 1H, H-4), 7.21 (AB, J = 6.5 Hz, 1H, H-5), 4.31 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 1.43 (s, 9H, 2-C(CH_3)$_3$), 1.37 (s, 9H, 7-C(CH_3)$_3$), 1.16 (t, J = 7.1 Hz, 3H, OCH_2CH_3), −1.40 (s, 6H, 12c,d-CH_3); ^{13}C NMR (C_6D_6) δ 167.2 (C=O), 145.6 (C-7), 144.8 (C-2), 139.5 (C-3a), 138.7 (C-5a), 135.6 (C-12b), 134.9 (C-12e), 133.2 (C-12a), 129.6 (C-12f), 128.7 (C-10), 127.8 (C-9), 126.4 (C-11), 125.5 (C-12), 123.0 (C-4), 122.3 (C-5), 122.0 (C-3), 121.3 (C-6), 119.8 (C-1), 118.5 (C-8), 61.4 (OCH_2CH_3), 36.0 (C-12d), 35.90 (C-12c), 35.85 (7-C(CH_3)$_3$), 35.83 (2-C(CH_3)$_3$), 31.2 (7-C(CH_3)$_3$), 31.0 (2-C(CH_3)$_3$), 17.98 and 17.96 (12c,d-CH_3), 14.84 (OCH_2CH_3); IR (film) ν 1717, 1252, 876, 767, 742 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 264 (14 800), 318 (21 000), 377 (19 200), 395 (24 900), 513 (4060), 630 (650); EIMS, m/z 466 (M^+); HRMS calcd for $C_{33}H_{38}O_2$ 466.2867, found 466.2875. Anal. Calcd: C, 84.94; H, 8.21. Found C, 84.97; H, 7.97.

4-Bromo-10-carboethoxy-2,7-di-*tert*-butyl-12c,12d-dimethyl-*trans*-12c,12d-dihydrobenzo[*e*]pyrene 30a and the 5-Bromo Isomer 30b. NBS (42.4 mg, 0.238 mmol) was added to a refluxing solution of the ester **24** (111 mg, 0.238 mmol) in dry dichloromethane (30 mL). The reaction mixture was refluxed for 30 min after which it was cooled to 22 °C and stirred for a further 3 h. Hexanes (60 mL) were added, and the solution was washed repeatedly with water (5 times 30 mL). The organic layer was then dried over $MgSO_4$, and the solvent was evaporated to give a red solid. This product was purified by chromatography on silica gel (deactivated with 5% H_2O) using 20:1 hexanes/ethyl acetate as eluant to give 127 mg (98%) of the product **30a**,**b** as a red powder along with a small amount of the dibromide **31**. The product could be further purified by recrystallization from acetonitrile to give red crystals, mp 105−107 °C, as a 3:1 mixture of the two isomers **30b**/**30a**, which could not be separated from each other: ^{1}H NMR (C_6D_6) [Peaks from the major 5-bromo isomer **30b** are assigned. *Indicates where major isomer peaks are indistinguishable from the minor isomer peaks] δ 9.90 (d, J = 1.7 Hz, 1H, H-9), 9.88 (d, J = 1.7 Hz), 8.73 (d, J = 8.7 Hz), 8.71 (d, J = 8.7 Hz, 1H, H-12), 8.58 (d, J = 1.1 Hz, 1H, H-8), 8.54 (d, J = 1.2 Hz), 8.48 (dd, J = 8.7 Hz, 1.7 Hz, 1H, H-11), 8.47 (dd, J = 8.6, 1.7 Hz), 8.42 (d, J = 1.1 Hz), 8.37 (d, J = 1.2 Hz, 1H, H-1), 8.13 (d, J = 1.2 Hz), 8.10 (d, J = 1.2 Hz, 1H, H-6), 7.38 (d, J = 0.9 Hz, 1H, H-4), 7.35 (d, J = 0.9 Hz), 7.26 (br s, 1H, H-3), 7.23 (br s), 4.29 (q, J = 7 Hz), 4.28 (q, J = 7 Hz, 2H, OCH_2CH_3), 1.41 (s), 1.36 (s, 1H, 2-C(CH_3)$_3$), 1.35 (s, 1H, 7-C(CH_3)$_3$), 1.30 (s), 1.142 (t, J = 7 Hz, 3H, OCH_2CH_3), 1.140 (t, J = 7 Hz), −1.35 (br s, 6H, 12c,d-CH_3)*; ^{13}C NMR (C_6D_6, major isomer (**30b**) peaks are assigned when possible) δ 166.97, 166.95 (C=O), 148.04 (C-7), 147.34, 147.32, 146.62 (C-2), 140.59, 139.83 (C-3a), 136.19 (C-12e), 136.03, 135.54, 135.40 (C-12b), 134.46 (C-5a), 133.72, 133.06, 133.01 (C-12a), 129.56, 129.52 (C-12f), 128.95 (C-10), 128.92, 127.91 (C-9), 127.64, 126.88 (C-11), 126.75 (C-4), 126.19, 125.67, 125.41 (C-12), 120.94 (C-3), 120.85, 120.26, 120.18 (C-6), 120.03, 119.78 (C-1), 118.80 (C-8), 118.56, 116.15, 115.45 (C-5), 61.50 (OCH_2CH_3), 39.48 (C-12d), 39.36, 36.36, 36.27, 36.25 (C-12c and one of 2,7-C(CH_3)$_3$), 35.88 (one of 2,7-C(CH_3)$_3$), 35.86, 30.95, 30.91 (2-C(CH_3)$_3$), 30.82, 30.78 (7-C(CH_3)$_3$), 18.25 (12c-CH_3), 18.21, 17.56, 17.52 (12d-CH_3), 14.80 (OCH_2CH_3), 14.69; IR (KBr) ν 1711, 1618, 1364, 1253, 1124, 1024, 869, 767 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 254 (12 900), 330 (2380), 345 (23 300), 381 (2910), 400 (39 800), 516 (5670), 627 (785); EIMS m/z 546 (M^+); HRMS calcd for $C_{33}H_{37}BrO_2$ 544.1977, found 544.1974. Anal. Calcd: C, 72.65; H, 6.83. Found: C, 72.11; H, 6.17.

10-Carboethoxy-2,7-di-*tert*-butyl-12c,12d-dimethyl-5-(2−5,-2′:5′,2″-terthienyl)-*trans*-12c,12d-dihydrobenzo[*e*]pyrene 32b and 4-Terthienyl Isomer 32a. $Pd_2(dba)_3$ (33 mg, 0.036 mmol) and dppf (32 mg, 0.058 mmol) were added to a solution of the mixed bromides **30** (438 mg, 0.73 mmol) and an excess of 2-tributylstannyl-5,2′:5′,2″-terthiophene **8**[12] (590 mg, 1.1 mmol) in THF (20 mL), and the solution was stirred under reflux for 72 h. The solution was cooled to 20 °C, stirred vigorously with aqueous KF (1 M, 10 mL) for 10 min, and then filtered through Celite, washing with THF. The product was then extracted into hexanes, which were washed well with water, dried ($MgSO_4$), and evaporated. The residue was then chromatographed on silica gel (deactivated with 5% H_2O) using first 20:1 hexanes/dichloromethane to elute the excess terthiophene followed by 20:1 hexanes/ethyl acetate and finally 10:1 hexanes/ethyl acetate to elute 400 mg (77%) of the product as a reddish brown solid which was a ∼3:1 mixture of isomers **32b**/**32a**. Recrystallization from acetonitrile gave red crystals, mp 149−150 °C: ^{1}H NMR (C_6D_6) [Peaks from the major isomer **32b** are assigned. *Indicates when the major isomer peaks are indistinguishable from the minor isomer] δ 10.00 (d, J = 1.6 Hz, 1H, H-9), 9.99 (d, J = 1.7 Hz), 8.84 (d, J = 8.7 Hz), 8.82 (d, J = 8.7 Hz, 1H, H-12), 8.70 (d, J = 1.1 Hz, 1H, H-8), 8.66 (d, J = 1.1 Hz), 8.54 (dd, J = 8.7, 1.6 Hz, 1H, H-11), 8.52−8.51 (m), 8.49 (d, J = 1.2 Hz, 1H, H-1), 8.47 (d, J = 1.2 Hz, 1H, H-6), 7.56 (d, J = 0.9 Hz, 1H, H-4), 7.54 (d, J = 0.9 Hz), 7.52 (s, 1H, H-3), 7.50 (t, J = 1.0 Hz), 7.25 (d, J = 3.7 Hz), 7.24 (d, J = 3.7 Hz, 1H, H-14), 7.14 (d, J = 3.5 Hz), 7.13 (d, J = 3.6 Hz, 1H, H-15), 7.01−6.98 (m, 2H, H-18,24)*, 6.89 (d, J = 3.7 Hz), 6.88 (d, J = 6.7 Hz, 1H, H-19), 6.73 (dd, J = 5.1, 1.1 Hz), 6.72 (dd, J = 5.1, 1.1 Hz, 1H, H-22), 6.660 (dd, J = 5.2, 3.6 Hz), 6.658 (dd, J = 5.1, 3.5 Hz, 1H, H-23), 4.35−4.26 (m, 2H, OCH_2CH_3)*, 1.44 (s, 9H, 2-C(CH_3)$_3$), 1.42 (s), 1.38 (s), 1.35 (s, 9H, 7-C(CH_3)$_3$), 1.16 (t, J = 7.2 Hz, 3H, OCH_2CH_3)*, −1.22 (s), −1.23 (s, 3H, 12d-CH_3), −1.25 (s), −1.26 (s, 3H, 12c-CH_3); ^{13}C NMR (C_6D_6) [peaks from the major isomer **32b** are assigned where identifiable] δ 167.1 (C=O), 147.3 (C-2), 146.54, 146.48, 145.8 (C-7), 143.6 (C-13), 139.3, 138.5 (C-3a), 137.9 (C-21), 137.8, 137.7 (C-16), 137.20 (C-17), 137.18, 137.0, 136.9 (C-20), 136.5 (C-12e), 136.1 (C-5a), 135.81, 135.76, 135.3, 135.1 (C-12b), 133.3, 133.1 (C-12a), 129.8 (C-12f), 128.5−128.3 (C-14,23), 128.0 (C-9), 127.9, 127.7, 126.7 (C-11), 126.6, 125.99 (C-5), 125.97 (C-4), 125.7, 125.4, 125.3 (C-12), 125.0 (C-22), 124.94, 124.91 (C-24/ 18), 124.7 (C-15), 124.5 (C-18/24), 121.9 (C-3), 121.2, 120.0 (C-1), 119.8, 119.1 (C-6), 118.7 (C-8), 61.5 (OCH_2CH_3), 37.3 (C-12d), 37.2, 36.31, 36.30 (7-C(CH_3)$_3$), 36.1, 35.92 (2-C(CH_3)$_3$), 35.88 (C-12c), 35.87, 35.3, 31.09, 31.07 (2-C(CH_3)$_3$), 30.96 (7-C(CH_3)$_3$), 30.93, 18.52 (12c/d-CH_3), 18.49, 18.41, 18.39 (12c/d-CH_3), 14.8 (OCH_2CH_3), 14.7; IR (film) ν 3066, 1715, 1251, 795, 767, 740, 694 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 251 (2100), 319 sh (22 600), 420 (49 300), 524 (7800), 645 (1000); EIMS m/z 712 (M^+); HRMS calcd for $C_{45}H_{44}O_2S_3$ 712.2503, found 712.2527. Anal. Calcd: C, 75.80; H, 6.33. Found: C, 75.51; H, 6.54.

2,7-Di-*tert*-butyl-12c,12d-dimethyl-5-(2−5,2′:5′,2″-terthienyl)-10-[(2−5,2′:5′,2″-terthienyl)carbonyl]-*trans*-12c,12d-dihydrobenzo[*e*]pyrene 39b and the 4-Terthienyl Isomer 39a. *n*-Butyl lithium (0.34 μL, 2.5 M) was added to a solution of the terthiophene **8** (R = H) (21.2 mg, 0.085 mmol) in dry THF (5 mL) at −78 °C. The solution was warmed to −30 °C over 30 min and then was recooled to −78 °C, and the Weinreb amide **37a**,**b** (42.4 mg, 0.058 mmol) was added in dry THF (2 mL). The solution warmed to ∼22 °C while stirring for 2 h. It was then

quenched with 1 M HCl and extracted with hexanes and water. The organic layer was washed, dried ($MgSO_4$), and evaporated to give a dark red-brown solid. The product was purified by chromatography on silica gel (deactivated with 5% H_2O) using 10:1 hexanes/dichloromethane to elute any excess terthiophene and then 2:1 hexanes/dichloromethane to elute 55 mg (59%) of product **39** as a ~7:3 mixture of isomers **39b**/**39a** as a dark reddish brown powder. Recrystallization from acetonitrile gave mp 164−166 °C: ^{1}H NMR (C_6D_6) [Peaks from the major isomer are assigned. *Indicates where major isomer peaks are indistinguishable from the minor isomer peaks] δ 9.77 (d, J = 1.9 Hz, 1H, H-9)*, 8.82 (d, J = 8.8 Hz), 8.81 (d, J = 8.8 Hz, 1H, H-12), 8.68 (d, J = 1.0 Hz, 1H, H-8), 8.63 (d, J = 1.2 Hz), 8.59 (s), 8.545 (d, J = 1.2 Hz), 8.540 (d, J = 1.1 Hz, 1H, H-1), 8.50 (d, J = 1.1 Hz, 1H, H-6), 8.21 (dd, J = 8.5, 1.8 Hz), 8.22 (dd, J = 8.5, 1.8 Hz, 1H, H-11), 7.59 (d, J = 0.9 Hz, 1H, H-4), 7.58 (s), 7.57 (d, J = 3.8 Hz, 1H, H-27), 7.56 (d, J = 1.1 Hz, 1H, H-3)*, 7.52 (s), 7.27 (d, J = 3.7 Hz), 7.26 (d, J = 3.7 Hz, 1H, H-14), 7.15 (d, J = 3.7 Hz, 1H, H-15), 7.01−6.98 (m, 3H, H-22,35 and one of 19,18, 31,32)*, 6.90−6.87 (m, 3H, H-28, and two of 19,18,31,31)*, 6.80 (d, J = 3.7 Hz, 1H, one of H- 19,18,31,32), 6.78 (d, J = 3.8 Hz), 6.74−6.72 (m, 2H, H-24,37)*, 6.68−6.64 (m, 2H, H-36,23)*, 1.48 (s, 9H, 2-C$(CH_3)_3$), 1.46 (s), 1.39 (s), 1.37 (s, 9H, 7-C$(CH_3)_3$), −1.189 (s), −1.192 and −1.21(2s, 3H each, 12c,d-CH_3), −1.22 (s); ^{13}C NMR (C_6D_6, major isomer peaks are assigned where possible) δ 187.0 (C═O), 147.3 (C-7), 146.6, 146.5, 146.1, 145.9 (C-2), 143.6 (C-13), 143.12, 143.11, 139.3, 139.1, 138.6, 137.88, 137.85, 137.8, 137.4, 137.19, 137.17, 137.03, 136.99, 136.5, 136.20 (C-3a), 136.17, 136.1 (C-5a), 135.9 (C-27), 135.8, 135.7, 135.4, 135.2 (C-12b), 132.8, 132.6 (C-12a), 129.9 (C-12f), 129.6, 128.59, 128.56, 128.5, 127.4 (C-9), 127.2, 127.0, 126.7, 126.6 (C-11), 126.1 (C-5), 126.0 (C-4), 125.7, 125.6 (C-24 or 37), 125.5, 125.43, 125.38 (C-12), 125.3, 125.04 (C-37 or 24), 124.97, 124.9 (C-22 or 35), 124.8 (C-15), 124.6, 124.5 (C-35 or 22), 122.0 (C-3), 121.4, 120.0 (C-1), 119.9, 119.2 (C-6), 118.9 (C-8), 37.4 (C-12d), 37.3, 36.37, 36.35 (7-C$(CH_3)_3$), 36.1, 36.0, and 35.94 (C-12c, 2-C$(CH_3)_3$), 35.91, 31.12, 31.10, and 31.02 (2,7-C$(CH_3)_3$), 31.00, 18.62, and 18.48 (12c,d-CH_3), 18.59, 18.52; IR (film) ν 3066, 1621, 1456, 1435, 1362, 1341, 1271, 1258, 873, 836, 793, 736, 692 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 246 (30 700), 321 (27 500), 426 (69 300), 526 (8400), 647 (1700); EIMS m/z 914 (M^+); HRMS calcd for $C_{55}H_{46}OS_6$ 914.1872, found 914.1828. Anal. Calcd: C, 72.17; H, 5.06. Found: C, 71.56; H, 5.72.

2,7-Di-*tert*-butyl-5-(2−3″,4″-dihexyl-5,2′:5′,2″:5″,2‴:5‴,-2⁗-quinquethienyl)-10-[2-(3″,4″-dihexyl-5,2′:5′,2″:5″,2‴:5‴,-2⁗-quinquethienyl)carbonyl]-12c,12d-dimethyl-*trans*-12c,12d-dihydrobenzo[*e*]pyrene 40b and the 4-Quinquethienyl Isomer 40a. *n*-Butyl lithium (1.0 mL, 2.5M) was added to a bright yellow solution of the quinquethiophene **13** (1.484 g, 2.55 mmol) in dry THF (60 mL) at −78 °C. The solution changed from yellow to a reddish orange. After warming to −30 °C over 30 min, it was recooled to −78 °C, and then the Weinreb amide **38a**,**b** (337 mg, 0.318 mmol) was added in dry THF (5 mL), giving a dark red solution. The solution was warmed to ~22 °C while stirring for 2 h. It was quenched with 1 M HCl and extracted with hexanes and water. The hexane extract was dried ($MgSO_4$) and evaporated to give a dark red-brown solid, which was chromatographed on silica gel (deactivated with 5% H_2O) using 10:1 hexanes/dichloromethane to elute the excess quinquethiophene **13** and then 10:1 hexanes/ethyl acetate to elute 301 mg (60%) of the product **40** as a dark red-black powder. Recrystallization by adding methanol to a diethyl ether solution gave mp 91−94 °C, which was a ~3:1 mixture of isomers **40b**/**40a**: ^{1}H NMR (C_6D_6) [Peaks from the major isomer are assigned. *Indicates where major isomer peaks are indistinguishable from the minor isomer peaks] δ 9.77 (d, J = 1.9 Hz, 1H, H-9)*, 8.84−8.82 (m), 8.81 (d, J = 8.9 Hz, 1H, H-12), 8.69 (s, 1H, H-8), 8.64 (s), 8.59 (s), 8.55 (s), 8.54 (s, 1H, H-1), 8.51 (s, 1H, H-6), 8.23−8.20 (m, 1H, H-11)*, 7.59−7.51 (m, 3H, H-3,4,42)*, 7.29 (d, J = 3.7 Hz), 7.27 (d, J = 3.7 Hz, 1H), 7.22 (d, J = 3.6 Hz), 7.21 (d, J = 3.7 Hz, 1H), 7.14 (d, J = 3.8 Hz), 7.13 (d, J = 3.7 Hz, 1H), 7.10 (d, J = 3.3 Hz), 7.09 (d, J = 3.7 Hz, 1H), 7.04−6.98 (m, 6H)*, 6.97−6.94 (m, 3H)*, 6.72 (d, J = 5.1 Hz, 2H)*, 6.652 (dd, J = 5.1, 3.5 Hz), 6.65 (dd, J = 5.1, 3.6 Hz, 2H, H-59,38), 2.88−2.80 (m, 8H, H-61,67,73,79)*, 1.76−1.63 (m, 8H, H-62,68,74,80)*, 1.48 (s, 9H, 2-C$(CH_3)_3$), 1.47 (s), 1.44−1.40 (m, 8H, H-63,69,75,81)*, 1.40 (s), 1.39 (s), 1.38 (s, 9H, 7-C$(CH_3)_3$), 1.32−1.26 (m, 16H, H-64,65,70,71,76,77,82,83)*, 0.92−0.88 (m, 12H, H-66,72,78,84)*, −1.19 (s, 3H, 12d-CH_3)*, −1.21 (s, 3H, 12c-CH_3), −1.22 (s); ^{13}C NMR (C_6D_6, the major ^{13}C isomer peaks are assigned where possible) δ 187.0 (C═O), 147.3 (C-7), 146.6, 146.5 (C-2), 146.1, 146.0, 145.9, 143.7, 143.4, 143.2, 141.8, 141.6, 141.3, 141.2, 141.1, 139.3, 138.6, 138.34, 138.30, 138.12, 138.11, 137.82, 137.78, 137.72, 137.67, 137.0, 136.7, 136.5, 136.19, 136.16, 136.10, 135.93, 135.89, 135.8, 135.6, 135.4, 135.2, 132.8, 132.6, 131.5, 131.01, 130.97, 130.5, 129.9, 129.6, 128.9, 128.7, 128.6, 128.50, 128.49, 128.4, 128.3, 128.2, 127.9, 127.8, 127.62, 127.60, 127.57, 127.5, 127.4 (C-9), 127.0, 126.9 (C-11), 126.7, 126.6, 126.1, 126.0 (C-12), 125.7, 125.5, 125.4, 125.3, 125.2, 125.1, 124.9, 124.8, 124.71, 124.69, 124.62, 124.57, 124.5, 122.0, 121.4, 120.0 (C-1), 119.9, 119.2 (C-6), 118.9 (C-8), 37.4 (C-12d), 37.3, 36.38, 36.36 (7-C$(CH_3)_3$), 36.1, 36.0 (C-12c), 35.94 (2-C$(CH_3)_3$), 35.92, 32.23, and 32.19 and 23.38 and 23.36 (C-64,65,70,71,76,77,82,83), 31.49 and 31.46 and 31.44 and 31.37 (C-62,68,74,81), 31.14, 31.11 (2-C$(CH_3)_3$), 31.05 (7-C-$(CH_3)_3$), 31.02, 30.4, and 30.3 (C-63,69,75,81), 29.1 and 29.0 (C-61,67,73,79), 18.63 (12c-CH_3), 18.60, 18.52, 18.48 (12d-CH_3), 14.7 and 14.6 (C-66,72,78,84); IR (film) ν 3066, 1622, 1436, 1273, 1054, 792, 737, 691 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 248 (43 900), 337 sh (44 200), 433 (99 500), 655 (1850); LSIMS m/z, 1580 (M^+). Anal. Calcd for $C_{95}H_{102}OS_{10}$: C, 72.19; H, 6.50. Found: C, 71.80; H, 6.71.

7-*tert*-Butyl-10b,10c-dimethyl-4,9-di-(2−5,2′:5′,2″-terthienyl)-2-naphthoyl-*trans*-10b,10c-dihydropyrene 53. $Pd_2(dba)_3$ (5 mg, 0.005 mmol) and dppf (10 mg, 0.018 mmol) were added to a solution of the dibromide **47** (28 mg, 0.047 mmol) and 2-tributylstannyl- 5,2′:5′,2″-terthiophene **8**[12] (0.126 mg, 0.234 mmol) in dry THF (10 mL), which was then refluxed for 18 h. After cooling to 21 °C, aqueous KF (10 mL) was added, and stirring was continued for a further 20 min. Hexanes/diethyl ether (1:1) and water were then added, and the organic extract was washed, dried ($MgSO_4$), filtered through Celite, and concentrated. The residue was chromatographed on silica gel (deactivated with 5% H_2O) using first 20:1 hexanes/ethyl acetate to elute excess terthiophene and then 10:1 hexanes/ethyl acetate to elute 40 mg (91%) of the product **53**, which on recrystallization from acetonitrile gave a dark green brown powder, mp 218−220 °C: ^{1}H NMR $CDCl_3$) δ 9.53 (d, J = 0.8 Hz, 1H, H-3), 9.15 (d, J = 1.1 Hz, 1H, H-8), 9.05 (s, 1H, H-1), 8.78 (s, 1H, H-10), 8.62 (s, 1H, H-5), 8.57 (s, 1H, H-6), 8.16 (dd, J = 8.6, 0.8 Hz, 1H, H-20), 8.10 (d, J = 8.3 Hz, 1H, H-15), 8.01 (d, J = 8.4 Hz, 1H, H-17), 7.87 (dd, J = 7.0, 1.2 Hz, 1H, H-13), 7.66 (dd, J = 8.3, 7.0, 1H, H-14), 7.56 (m, 1H, H-18), 7.49 (d, J = 3.8 Hz, 1H, H-39), 7.47 (m, H, H-19), 7.39 (d, J = 3.8 Hz, 1H, H-40), 7.36 (d, J = 3.8 Hz, 1H, H-27), 7.27−7.21 (m, 6H), 7.16−7.15 (m, 3H), 7.08−7.05 (m, 2H), 1.68 (s, 9H, 7-C$(CH_3)_3$), −3.30 (s, 3H, 10b-CH_3), −3.37 (s, 3H, 10d-CH_3); ^{13}C NMR ($CDCl_3$) δ 198.7 (C═O), 152.2 (C-7), 143.0 (C-38), 142.8 (C-26), 142.3 (C-5a), 138.7 (C-29), 138.6 (C-10d), 138.32 (C-12), 138.25 (C-41), 137.40, 137.37, 136.71, 136.61, 136.5 (C-42), 136.4, 135.1 (C-10a), 134.1 (C-16), 132.8 (C-4), 131.54 (C-21), 131.49 (C-3a), 131.1 (C-10), 130.9 (C-15), 130.6 (C-2), 129.1 (C-27), 128.7 (C-17), 128.5 (C-39), 128.18, 128.16, 127.7 (C-13), 127.4 (C-1), 127.3 (C-9), 127.2 (C-19), 126.5 (C-18), 126.4 (C-20), 125.9 (C-3), 125.5 (C-5), 125.0 (C-14), 124.8, 124.74, 124.68, 124.65, 124.6, 124.5

(C-40), 124.03, 124.01, 122.8 (C-6), 121.5 (C-8), 36.9 (7-$\underline{C}(CH_3)_3$), 32.2 (C-10c), 32.1 (C-10b), 31.1 (7-C($\underline{C}H_3)_3$), 17.1 ($\overline{1}$0c-CH_3), 15.90 (10d-CH_3); IR (film) ν 3065, 1636, 1548, 1282, 1236, 1183, 1134, 1074, 792, 692 cm^{-1}; UV−vis (cyclohexane/dichloromethane (1:1)) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 248 sh (59 800), 371 (47 200), 456 (78 200), 568 (16 200), 703 (1600); LSIMS m/z 935.1 (M^+); HRMS calcd for $C_{57}H_{43}OS_6$ (M + H) 935.1638, found 935.1636.

7-*tert*-Butyl-4,9-di-(2−3″,4″-dihexyl-5,2′:5′,2″:5″,2‴:5‴,-2⁗-quinquethienyl)-10b,10c-dimethyl-2-naphthoyl-*trans*-10b,-10c-dihydropyrene 54. $Pd_2(dba)_3$ (9 mg, 0.01 mmol) and dppf (10 mg, 0.02 mmol) were added to a solution of the dibromide **47** (115 mg, 0.19 mmol) and the quinquethiophene **12**[12,13] (384 mg, 0.44 mmol) in dry THF (5 mL), and the solution was refluxed for 18 h. Additional $Pd_2(dba)_3$ (9 mg, 0.01 mmol) was then added and reflux continued for 12 more hous. After cooling, aqueous KF (10 mL) was added and the reaction mixture was stirred for 15 min. It was then extracted with ether and water, and the extract was washed, dried ($MgSO_4$), filtered through Celite, and evaporated to give a dark brown-black solid. This was chromatographed on silica gel (deactivated with 5% H_2O) using 20:1 hexanes/ethyl acetate as eluant to elute first excess quinquethiophene **13**, second a mixture of mono addition products (28 mg), and third 171 mg (56%) of the desired product **54**, which on recrystallization from cyclohexane gave a dark brown-black powder, mp 98−100 °C: ^{1}H NMR ($CDCl_3$) δ 9.54 (s, 1H, H-3), 9.16 (s, 1H, H-8), 9.05 (s, 1H, H-1), 8.79 (s, 1H, H-10), 8.63 (s, 1H, H-5), 8.58 (s, 1H, H-6), 8.17 (d, J = 8.3 Hz, 1H, H-20), 8.09 (d, J = 8.3 Hz, 1H, H-15), 8.01 (d, J = 8.5 Hz, 1H, H-17), 7.86 (dd, J = 7.0, 1.0 Hz, 1H, H-13), 7.67 (dd, J = 8.2, 7.0 Hz, 1H, H-14), 7.59−7.55 (m, 1H, H-18), 7.50 (d, J = 3.7 Hz, 1H, H-47), 7.49−7.45 (m, 1H, H-19), 7.40 (d, J = 3.7 Hz, 1H, H-48), 7.37 (d, J = 3.7 Hz, 1H, H-27), 7.27 (d, J = 3.7 Hz, 1H), 7.24 (d, J = 3.7 Hz, 1H, H-28) 7.24−7.23 (m, 1H), 7.23−7.19 (m, 4H), 7.15 (t, J = 3.6 Hz, 2H), 7.12 (dd, J = 3.7, 3.1 Hz, 2H), 7.07 (dd, J = 5.5, 3.7 Hz, 2H), 7.06−7.03 (m, 2H), 2.81−2.73 (m, 8H, H-65,71,77,83), 1.68 (s, 9H, 7-C($CH_3)_3$), 1.66−1.59 (m, 8H, H-66,72,78,84), 1.51−1.47 (m, 8H, H-67,73,79,85), 1.41−1.34 (m, 16H, H-68,69,74,75,80,81,86,87), 0.96−0.91 (m, 12H, H-70,76,82,88), −3.29 (s, 3H, 10b-CH_3), −3.36 (s, 3H, 10c-CH_3); ^{13}C NMR ($CDCl_3$) δ 198.7 (C═O), 152.1 (C-7), 142.9 (C-46), 142.7 (C-26), 142.3 (C-5a), 140.6, 138.7, 138.6, 138.3 (C-10d), 137.4, 137.32, 137.27, 137.2, 135.6, 135.5, 135.29, 135.27, 135.0 (10a), 134.0, 132.8 (C-4), 131.52, 131.49 (C-3a), 131.1 (C-10), 130.9 (C-15), 130.6, 130.1, 130.01, 129.99, 129.1 (C-27), 128.7 (C-17), 128.5 (C-47), 128.1, 127.7 (C-13), 127.5 (C-1), 127.3 (C-9), 127.2 (C-19), 126.7, 126.64, 126.59, 126.55 (C-18), 126.3 (C-20), 125.9 (C-3), 125.5 (C-5), 124.9 (C-14), 124.7, 124.5, 124.4 (C-48), 124.3, 124.2, 124.1, 123.9, 122.8 (C-6), 121.5 (C-8), 36.9 (7-C($CH_3)_3$), 32.2 (C-10b), 32.0 (C-10c), 31.8 (7-C($CH_3)_3$), 31.75, 31.71, 30.9 (C-66), 29.85 and 29.81 (C-67,73,79,85), 28.51 and 28.47 (C-65,71,77,83), 22.89 and 22.88, 22.85 (C-68,69), 17.1 (10c-CH_3), 15.9 (10b-CH_3), 14.36 and 14.33 and 14.32 (C-70,76,82,88); IR (film) ν 3065, 1640, 1548, 1462, 1282, 1236, 1183, 1134, 1073, 791, 690 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 221 (82 100), 249 sh (35 600), 382 (57 800), 459 (81 800), 566 (18 900), 703 (1600); LSIMS m/z 1600 (M^+); HRMS calcd for $C_{97}H_{99}OS_{10}$ (M + H) 1599.4903, found 1599.4935. Anal. Calcd for $C_{97}H_{98}OS_{10}$: C, 72.79; H, 6.17. Found: C, 72.82; H, 6.25.

7-*tert*-Butyl-10b,10c-dimethyl-4,9-diphenyl-2-naphthoyl-*trans*-10b,10c-dihydropyrene 57. Palladium tetrakis(triphenylphosphine) (11 mg, 0.01 mmol) was added to a solution of the bromide **47** (111 mg, 0.19 mmol) and phenylboronic acid (68 mg, 0.56 mmol) in dimethoxyethane (5 mL) and saturated aqueous Na_2CO_3 (4 mL). The solution was then refluxed for 24 h with vigorous stirring. The product was then poured into hexanes, washed well with water, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (deactivated with 5% H_2O) using 10:1 hexanes/ethyl acetate to elute 115 mg (100%) of product **57** as a purple solid, which on recrystallization from methanol gave mp 203−204 °C: ^{1}H NMR (C_6D_6) δ 9.11 (s, 1H, H-3), 9.01 (s, 1H, H-1), 8.69 (s, 1H, H-8), 8.66 (s, 1H, H-10), 8.56 (s, 1H, H-6), 8.51 (s, 1H, H-5), 8.12 (d, J = 8.6 Hz, 1H, H-20), 8.03 (d, J = 8.2 Hz, 1H, H-15), 7.98 (d, J = 8.2 Hz, 1H, H-17), 7.79 (brd, J = 7.2 Hz, 3H, H-13,33,37), 7.70 (d, J=6.7 Hz, 2H, H-31,27), 7.63−7.57 (m, 3H, H-34,35,36), 7.56−7.48 (m, 2H, H-14,18), 7.48−7.40 (m, 4H, H-19,28,29,30), 1.60 (s, 9H, 7-C($CH_3)_3$), −3.40 (s, 3H, 10c-CH_3), −3.47 (s, 3H, 10b-CH_3); ^{13}C NMR (C_6D_6) δ 198.9 (C-11), 151.4 (C-7), 142.1 (C-5a), 141.9 (C-32), 141.7 (C-26), 141.5 (C-4), 138.7 (C-10d), 138.5, 135.7 (C-9), 134.8 (C-10a), 134.0 (C-16), 131.7 (C-3a), 131.6, 131.2 (C-33,37), 131.1 (C-10), 131.0 (C-27,31), 130.7 (C-15), 1230.0, 128.62 (C-17), 128.56 (C-34,36), 128.48 (C-28,30), 127.7, 127.6 (C-29), 127.5 (C-13), 127.0 (C-19), 126.7 (C-1), 126.43, 126.38 (C-20), 125.8 (C-3), 125.7 (C-5), 124.8 (C-35), 122.1 (C-6), 121.1 (C-8), 36.7 (7-$\underline{C}(CH_3)_3$), 31.8 (7-C($\underline{C}H_3)_3$), 31.7 (C-10b), 31.5 (C-10c), 16.8 ($\overline{1}$0b-CH_3), 15.5 (10c-$\underline{C}H_3$); IR (film) ν 3055, 1640, 1547, 1284, 1234, 1137, 783, 701 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 222 (67 500), 273 (16 900), 363 (67 400), 396 (25 200), 419 (49 800), 537 (13 700), 676 (640); EI MS m/z 594 (M^+); HRMS calcd for $C_{45}H_{35}O$ 594.292, found 594.293.

Visible Light Opening Experiments To Form the CPDs. These were performed using a 500 W household tungsten−halogen lamp (8500 lm) as the light source with a 490 nm cut off filter unless otherwise stated. Samples were irradiated while in an ice cooled water bath (∼5 °C) unless otherwise stated.

For NMR samples, 5−20 mg of sample was dissolved in the NMR solvent. Argon was bubbled through the solution for about 1 min, and then the NMR tube was capped and wrapped with film. The tube was placed in a 5 °C bath and was irradiated until the color faded (∼5−10 min). The NMR spectrum was then quickly recorded.

For UV samples, ∼1 mg of sample was dissolved in solvent, and 5× and 10× dilutions were made. The three sets of solutions were placed in quartz UV−vis cells, and argon was bubbled through for 2 min. The samples were cooled to ∼5 °C and irradiated as above until the color faded (∼1−5 min). The UV−vis spectra of the three sets of solution was not then immediately measured.

CPD 7′: ^{1}H NMR (C_6D_6) δ 7.73−7.71 (AA′XX′,1H), 7.29 (d, J = 2.1 Hz, 2H), 7.26−7.24 (AA′XX′, 2H), 7.04 (d, J = 2.1 Hz, 2H), 6.97 (d, J = 3.8 Hz, 2H), 6.90 (d, J = 3.8 Hz, 2H), 6.88 (dd, J = 3.6, 1.1 Hz, 2H), 6.78 (d, J = 3.8 Hz, 2H), 6.72 (d, J = 3.8 Hz, 2H), 6.67 (dd, J = 5.0, 1.0 Hz, 2H), 6.60 (dd, J = 5.0, 3.6 Hz, 2H), 1.68 (s, 6H), 1.15 (s, 18H); ^{13}C NMR (C_6D_6) δ 150.7, 145.2, 145.1, 141.0, 140.8, 140.3, 138.7, 137.8, 136.94, 136.93, 136.5, 131.4, 130.7, 129.2, 129.1, 128.9, 126.5, 125.2, 125.1, 124.9, 124.4, 124.0, 34.6, 31.6, 30.6, 19.8; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 250 (49 800), 380 (53 900).

CPD 14′: ^{1}H NMR (360 MHz, C_6D_6) δ 7.7−6.6 (m, 2H), 7.23 (d, J = 2.1 Hz, 2H), 7.22−7.19 (m, 2H), 6.99 (d, J = 2.1 Hz, 2H), 6.96−6.91 (m, 8H), 6.88−6.86 (m, 6H), 6.69 (dd, J = 5.1, 1.1 Hz, 2H), 6.60 (dd, J = 5.1, 3.5 Hz, 2H), 2.76−2.70 (m, 8H), 1.61 (s, 6H), 1.62−1.56 (m, 8H), 1.38−1.29 (m, 8H), 1.24−1.17 (m, 16H), 1.12 (s, 18H), 0.85−0.79 (m, 12H); UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 249 (83 900), 408 (83 800).

CPD 24′: ^{1}H NMR (C_6D_6) δ 8.75 (d, J = 1.9 Hz, 1H), 8.21 (dd, J = 8.1, 1.9 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.06 (d, J = 2.2 Hz, 1H), 6.94 (d, J = 2.2 Hz, 1H), 6.86 (d, J = 2.2, 1H), 6.85 (d, J = 2.1 Hz, 1H), 6.35 (s, 2H), 4.22 (dq, J = 10.8, 7.1 Hz), 4.14 (dq, J = 10.8, 7.1 Hz), 1.47 (s, 3H), 1.44 (s, 3H), 1.24 (s, 9H), 1.17 (s, 9H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (C_6D_6) δ 166.5, 151.7, 151.3, 149.3, 145.1, 140.8, 140.4, 140.0, 137.9, 137.8, 133.1, 132.9, 131.6, 130.6, 130.3, 129.6, 129.0, 123.9, 123.6,

61.3, 35.4, 35.3, 34.53, 34.48, 31.8, 31.7, 19.7, 19.5, 14.71; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 213 (29 200), 226 (29 200), 251 (30 600).

CPD 40′: ^{1}H NMR (C_6D_6) δ 8.53 (br s, 1H)*, 7.91−7.89 (m, 1H)*, 7.72 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 3.9 Hz, 1H)*, 7.35 (s, 1H), 7.21−7.19 (m, 1H)*, 7.18−7.17 (m, 1H)*, 7.11−7.10 (m, 1H)*, 7.06−6.94 (m, 13H)*, 6.87 (d, J = 4.0 Hz, 1H), 6.72 (d, J = 5.0 Hz, 2H)*, 6.66−6.64 (m, 2H)*, 2.86−2.80 (m, 8H)*, 1.76−1.61 (m, 8H)*, 1.56 (s, 3H)*, 1.46 (s, 3H), 1.45−1.38 (m, 8H)*, 1.30 (s, 9H), 1.29−1.26 (m, 16H)*, 1.16 (s, 9H), 0.94−0.86 (s, 12H)*. Minor isomer where distinguishable from the major isomer: ^{1}H NMR (C_6D_6) δ 7.69 (d, J = 7.8 Hz, 1H), 7.39 (s, 1H), 6.88 (d, J = 4.0 Hz, 1H),1.47 (s, 3H), 1.24 (s, 9H), 1.22 (s, 9H); UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 245 (56 700), 431 (89 200).

CPD 53′: ^{1}H NMR ($CDCl_3$) δ 8.06 (dd, J = 7.0, 2.1 Hz, 1H), 7.97 (d, J = 8.0, 1H), 7.91−7.89 (m, 1H), 7.63 (d, J = 1.6 Hz, 1H), 7.56 (dd, J = 7.0, 1.1 Hz, 1H), 7.54−7.49 (m, 3H), 7.37 (d, J = 1.6 Hz, 1H), 7.24−7.22 (m, 2H), 7.20−7.18 (m, 2H), 7.14−7.07 (m, 5H), 7.07 (d, J = 2.0 Hz, 1H), 7.06 (d, J = 2.0 Hz, 1H), 7.05−7.01 (m, 2H), 7.00 (d, J = 3.7 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.75 (s, 1H), 6.65 (s, 1H), 1.64 (s, 3H), 1.60 (s, 3H), 1.26 (s, 9H); UV−vis (1:1 cyclohexane/dichloromethane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 252 (41 000), 310 (23 100), 388 (56 800), 446 (43 100).

CPD 54′: ^{1}H NMR ($CDCl_3$) δ 8.10−8.09 (m, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.92−7.90 (m, 1H), 7.66 (d, J = 1.5 Hz, 1H), 7.58 (d, J = 7 Hz, 1H), 7.55−7.50 (m, 3H), 7.41 (d, J = 1.2 Hz, 1H), 7.24 (d, J = 4.9 Hz, 2H), 7.21−7.20 (m, 2H), 7.15−7.14 (m, 5H), 7.10−7.0 (m, 10H), 6.94 (d, J = 1.9 Hz, 1H), 6.78 (s, 1H), 6.68 (s, 1H), 2.77−2.73 (m, 8H), 1.67 (s, 3H), 1.64 (s, 3H), 1.62−1.59 (m, 8H), 1.48−1.41 (m, 8H), 1.39−1.36 (m, 16H), 1.29 (s, 9H), 1.0−0.92 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 196.5, 152.5, 152.2, 144.7, 144.5, 140.64, 140.61, 139.8, 139.5, 139.2, 139.0, 138.6, 137.6, 137.34, 137.32, 137.25, 137.1, 136.8, 136.6, 136.2, 135.7, 135.6, 135.3, 135.2, 133.9, 131.3, 131.1, 130.3, 130.08, 130.06, 129.94, 129.91, 129.2, 128.6, 128.1, 127.7, 127.5, 127.3, 127.2, 126.64, 126.58, 126.0, 125.8, 125.1, 124.7, 124.6, 124.4, 124.3, 124.2, 124.0, 123.9, 34.5, 31.8, 31.7, 31.5, 30.9, 29.8, 28.5, 27.1, 22.9, 20.7, 20.0, 14.34, 14.32; UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 218 (86 900), 398 (60 700), 434 (63 300).

CPD 57′: ^{1}H NMR (C_6D_6) δ 8.02 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.87−7.85 (br d, J = 7.3 Hz, 1H), 7.56−7.51 (m, 4H), 7.49−7.42 (m, 4H), 7.36−7.29 (m, 7H), 7.17 (d, J = 1.4 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 6.67 (s, 1H), 6.58 (d, J = 2.0 Hz, 1H), 6.52 (s, 1H), 1.76 (s, 3H), 1.73 (s, 3H), 1.17 (s, 9H); UV−vis (cyclohexane) λ_{max} (ε_{max}, L mol^{-1} cm^{-1}) nm, 222 (82 800), 272 (47 800), 307 (27 800).

UV Closing Experiments. The "visible light opened samples" from above were irradiated with a 3 W low pressure Hg(Ar) pencil light (Oriel 6035, mainly 254 nm) while being cooled with an electric fan.

Thermal Closing Experiments. The "visible light opened samples" from above were placed in the NMR probe at the appropriate temperature, and integrations of like signals (e.g., internal methyl protons) were obtained for several sets of signals. The logarithmic plot of the molar fraction of the closed form against time at each temperature then gave the rate constant at that temperature. Arrhenius and Eyring plots were then used to obtain E_{act}, ln A, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ data, which are reported in the Supporting Information.

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Supporting Information Available: Syntheses of compounds **5**, **6**, **9**, **11**, **15**, **22**, **23**, **25**, **31**, **33**, **34**, **35**, **36**, **37**, **38**, **41**, **43**, **44**, **45**, **48**, **49**, **50**, **51**, **55**, and **56** and CPDs **15′**, **25′**, **30′**, **31′**, **32′**, **33′**, **34′**, **36′**, **38′**, **39′**, **41′**, and **55′**, general synthetic experimental conditions, numbering systems used for NMR assignments, ^{1}H and ^{13}C NMR spectra for all new DHP and CPD compounds, the UV−visible absorption comparison of green and red laser pointer opening of a thin film of **54**, a comparison of the visible light opening rates vs BDHP **4** for the compounds in Table 1 (relative rate data), a comparison of UV closing rates vs BDHP **4′** for **14′**, **40′** and **54′**, thermal closing rate data for the compounds of Table 2, including thermodynamic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.