

## MIT Open Access Articles

*Photoalignment Layers for Liquid Crystals  
from the Di- $\pi$ -methane Rearrangement*

The MIT Faculty has made this article openly available. *Please share*  
how this access benefits you. Your story matters.

**Citation:** Cox, Jason R., Jeffrey H. Simpson, and Timothy M. Swager. "Photoalignment Layers for Liquid Crystals from the Di- $\pi$ -methane Rearrangement." *Journal of the American Chemical Society* 135, no. 2 (January 16, 2013): 640-643.

**As Published:** <http://dx.doi.org/10.1021/ja312090p>

**Publisher:** American Chemical Society (ACS)

**Persistent URL:** <http://hdl.handle.net/1721.1/84617>

**Version:** Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

**Terms of Use:** Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.



**Photoalignment Layers for Liquid Crystals from the Di-n-Methane Rearrangement**

|                               |                                                                                                                                                                                                                                                               |
|-------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Journal:                      | <i>Journal of the American Chemical Society</i>                                                                                                                                                                                                               |
| Manuscript ID:                | Draft                                                                                                                                                                                                                                                         |
| Manuscript Type:              | Communication                                                                                                                                                                                                                                                 |
| Date Submitted by the Author: | n/a                                                                                                                                                                                                                                                           |
| Complete List of Authors:     | Cox, Jason; Massachusetts Institute of Technology, Chemistry<br>Simpson, Jeffrey; Massachusetts Institute of Technology, Chemistry<br>Swager, Timothy; Mass. Inst. of Tech., Chemistry; Massachusetts Institute of Technology, Department of Chemistry 18-597 |
|                               |                                                                                                                                                                                                                                                               |

SCHOLARONE™  
Manuscripts

# Photoalignment Layers for Liquid Crystals from the Di- $\pi$ -Methane Rearrangement

Jason R. Cox, Jeffrey H. Simpson, and Timothy M. Swager\*

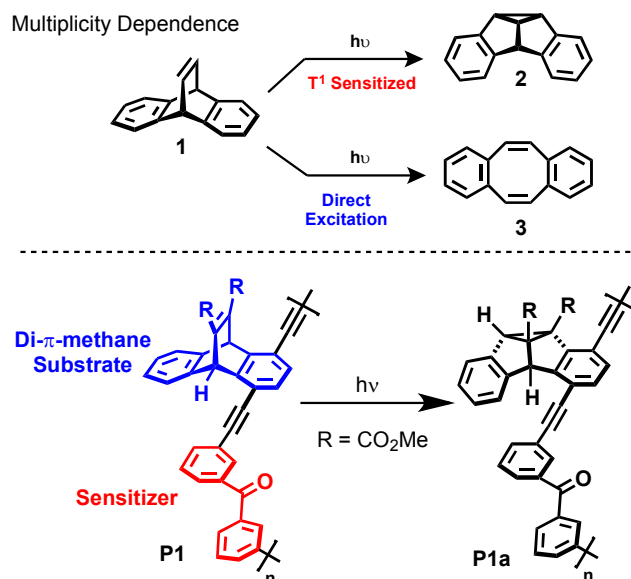
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information Placeholder

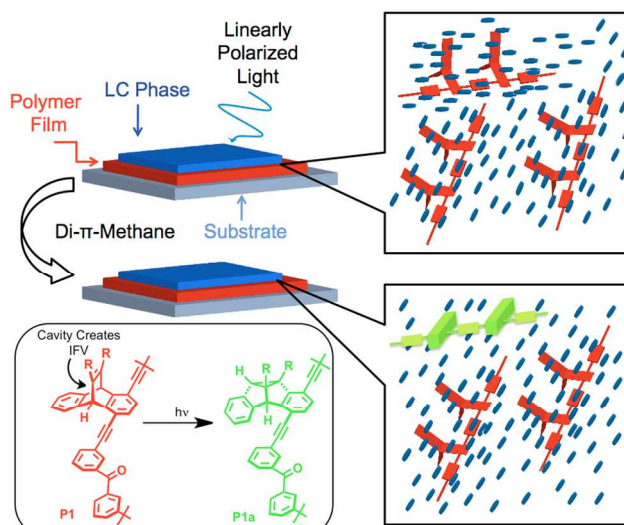
**ABSTRACT:** Photoalignment of nematic liquid crystals is demonstrated using a di- $\pi$ -methane rearrangement of a designed polymer. The alignment mechanism makes use of the strong coupling of the liquid crystal directors to dibenzobarrelene groups. The large structural changes that accompany photoisomerization effectively passivate segments of the polymer allowing the remaining dibenzobarrelene groups to dominate the director alignment. The photoisomerization requires triplet sensitization and the polymer was designed to have a uniaxially fixed rigid structure and rapid triplet energy transfer from the proximate benzophenone units to the dibenzobarrelene groups. The isomerization was observed to be regioselective and thin films showed alignment.

Devices that exploit the unique opto-electronic and self-assembling characteristics of liquid crystalline (LC) materials are a cornerstone of modern technology.<sup>1</sup> A majority of technologies require a uniform alignment of the LC phases – a challenge that traditionally has been met through the unidirectional ‘rubbing’ of polymeric substrates.<sup>2</sup> Despite the crude nature of this approach, it continues to be a dominant method to induce LC alignment. The rubbing approach, however, is not without disadvantages – specifically it can generate dust<sup>3</sup> and static charge at the interface of the substrate, is not compatible with surfaces with complex topologies, and an damage sensitive electronic components that are part of integrated devices.<sup>4</sup> To overcome this problem, non-contact alignment methods have been developed, the majority of which employ axis-selective photochemical transformations, to generate highly aligned LC phases.<sup>4,5</sup> Many of these approaches exploit well-known photochemical reactions such as the isomerization of unsaturated centers and photochemically allowed cycloaddition reactions. A conspicuously undeveloped photochemical reaction for this application is the well-known di- $\pi$ -methane rearrangement, which is a robust photochemical transformation that generates large shape changes in the molecular structure of the reactant (see Figure 1, 1→2).<sup>6</sup> To address the need for new efficient transformations that can create alignment layers, we report here the application of the di- $\pi$ -methane rearrangement to create films capable of alignment of nematic liquid crystals.

Zimmerman and coworkers described the di- $\pi$ -methane rearrangement in full-detail, yielding predictive measures for the determination of regioselectivity and the role of excited state multiplicity in the reaction mechanism.<sup>7</sup> These seminal works serve as a starting point for the design of a polymer capable of undergoing a regioselective di- $\pi$ -methane rearrangement. Drawing upon the ability of triptycene structures to enhance the alignment of LC



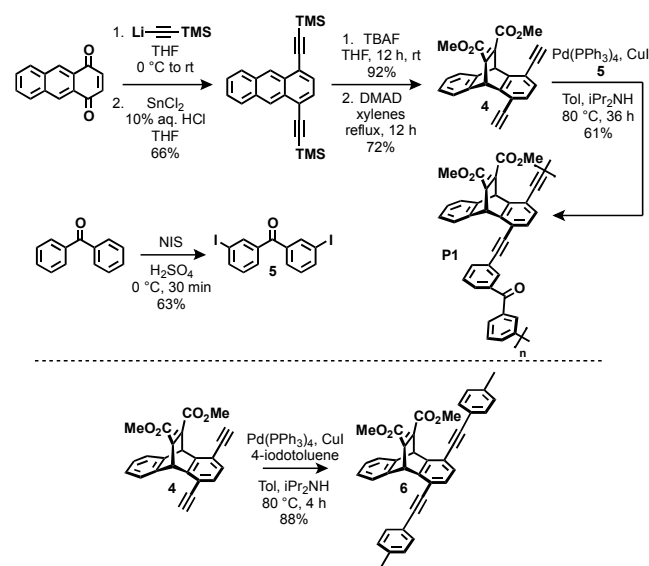
**Figure 1.** Photochemical behavior of dibenzobarrelene substrates<sup>6</sup> under direct and sensitized irradiation conditions (top). Polymeric di- $\pi$ -methane rearrangement of **P1** facilitated by intra-polymer triplet sensitization (bottom).



**Figure 2.** Schematic depiction of proposed photoalignment mechanism (Red/green barbed structures = **P1/P1a**) (Blue ellipsoids = LC molecules).

molecules through the minimization of internal free volume (IFV),<sup>8</sup> we envisioned that substituted dibenzobarrelene structures could provide similarly strong director field interactions with the LC phases (Figure 2). Upon photolysis, the expected semibullvalene-like products would exhibit diminished IFV, thus eliminating the alignment preferences of the dibenzobarrelenes.

**Scheme 1. Synthesis of Monomers (4, 5), Polymer (P1), and Model Compound (6)**



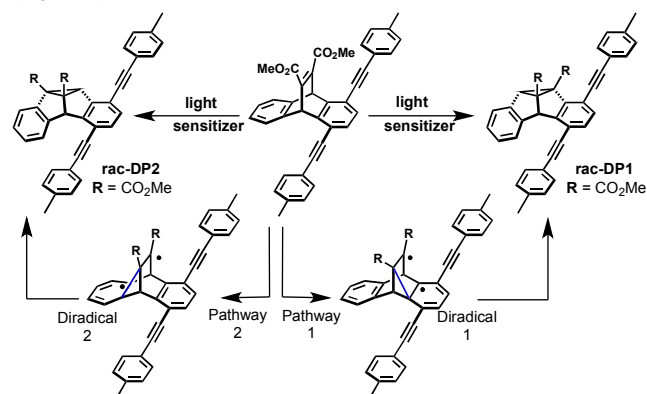
As shown in Figure 1 (top), the di-π-methane rearrangement of rigid structures such as dibenzobarrelene 2 proceeds through a triplet manifold whereas direct irradiation primarily yields 3.<sup>9</sup> Noting this behavior, we incorporated a triplet sensitizer in the polymer backbone directly adjacent to the di-π-methane substrate (Figure 1, P1). Such a design motif is attractive for two reasons: (1) the proximity of sensitizer and substrate enforces rapid energy transfer<sup>10</sup> and (2) once sensitization of the di-π-methane substrate is complete, newly formed benzophenone diradicals<sup>11</sup> can cross-link the film thereby yielding an insoluble polymeric layer between the LC layer and substrate. The first point is of critical importance given that the initial directional information imparted by photolysis with plane polarized light can be lost through energy transfer to non-nearest neighbors. Hence it is key that the molecular locations that absorb the light undergo the photoisomerization.

Our proposed photoalignment is schematically depicted in Figure 2 and operates as follows: (1) polarized light selectively excites benzophenone units with transition dipole moments oriented parallel to the electric vector of the exciting light, (2) rapid intersystem crossing (ISC) to the first triplet state, (3) fast energy transfer to adjacent di-π-methane units and (4) subsequent rearrangement. In thin films, such a cascade would result in a new surface landscape where molecules residing in the plane perpendicular to the exciting light would be left unreacted and still capable of strongly influencing the LC director through strong interactions with the dibenzobarrelene groups. The isomerized units lack the clefts that created the IFV and the strong interactions with the LC directors, thereby allowing the remaining P1 to dictate the direction of LC alignment.

The syntheses of monomers 4 and 5, as well as the synthesis of P1 are outlined in Scheme 1. The synthetic approaches to monomers 4 and 5 are straightforward, affording both components in reasonable yields via short synthetic sequences. The Sonogashira-Hagihara reaction was chosen to generate the target polymer P1 because it is a robust cross-coupling polymerization method for

the synthesis of poly(phenylene ethynyles) (PPEs).<sup>12</sup> A critical element of the design is that the polymer backbone rigidly fixes the dibenzobarrelene orienting groups along a given direction and similarly the passivated photoisomerized groups are locked in position. This is accomplished by a two fold connection through ethynyl linkages that uniaxially fixes the direction for monomer units in P1.

Prior to engaging directly into photochemical studies of P1, we conducted small molecule studies employing model compound 6 in order to gain insight into the photochemical behavior of this class of substrates. We were particularly interested in the implications of using unsymmetrically substituted barrelene scaffolds – such substrates could potentially yield two racemic photoproducts (Figure 3).

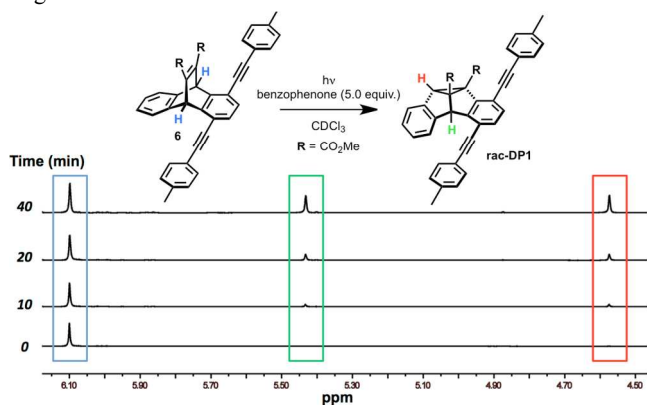


**Figure 3.** Postulated photochemical pathways available to model compound 6 after sensitized excitation.

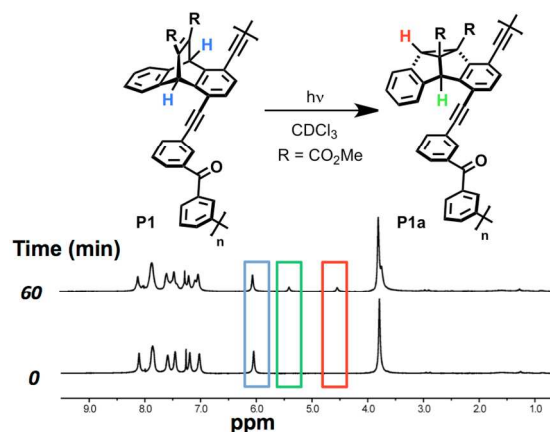
We surmised that the extended conjugation available to Diradical 1, would favor Pathway 1 thus yielding rac-DP1 as the major product. Upon sensitized photolysis of 6, only a single photoproduct was observed by <sup>1</sup>H NMR as shown in Figure 4. During the photolysis, we monitored the emergence of the two new methine resonances (Figure 4, shown as red and green), which was concomitant with a reduction of the original bridgehead methine (normalized in Figure 4, shown as blue). The new signals belong to the benzylic and doubly benzylic cyclopropyl methines that are part of the newly assembled semibullvalene-like structure. Gratifyingly, further 2D NMR analysis (see Supporting Information) revealed that the newly formed product was rac-DP1 as initially predicted.

Having established that the reaction proceeds efficiently and selectivity at the small molecule level, we turned our attention to the photochemical behavior of P1. For these reactions, the photochemistry was performed under ambient conditions – without the exclusion of oxygen from the reaction vessel. Conducting photoalignment operations under strictly inert conditions is not optimal for industrial processes. We hypothesized that the proximity of sensitizer and substrate would facilitate the transformation despite the fact that such reactions typically require rigorous exclusion of oxygen to prevent quenching of the triplet state by oxygen. In addition, we were interested in verifying that the observed product distribution at the small molecule level translated to P1. In order to generate robust photoalignment layers based on the mechanism depicted in Figure 2, it is necessary to ensure the formation of rac-DP1. The molecular structure of this product contains two methyl ester moieties project in a fashion that can block interactions between liquid crystal molecules and the plane created by the rigid phenyl-ethynyl linkages – effectively eliminating strong director field interactions. The alternative photoproduct, rac-DP2, projects the methyl ester groups away from the rigid

PPE backbone and therefore could possibly generate competitive alignment sites.



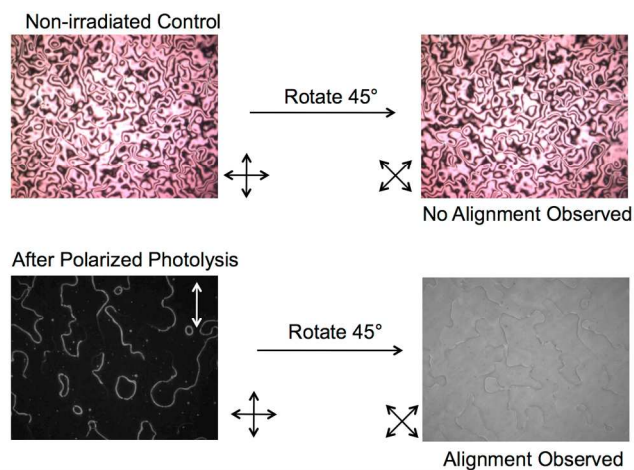
**Figure 4.** Di- $\pi$ -methane rearrangement of model compound **6** (top). Time-elapsing  $^1\text{H}$  NMR spectra recorded during the sensitized photolysis of **6** (bottom). The intensity is normalized to the resonance at 6.1 ppm.



**Figure 5.** Di- $\pi$ -methane rearrangement of **P1** (top). Time-elapsing  $^1\text{H}$  NMR spectra of the reaction (bottom).

As shown in Figure 5, the rearrangement of **P1** takes place smoothly and cleanly in the presence of oxygen. Similar to the regioselectivity observed with model compound **6**, only a single set of product methines are evident – lending credence to the notion that the reaction proceeds with a high level of regioselectivity.

With a firm understanding of the photochemical behavior of **P1**, we directed our efforts towards the fabrication of LC alignment layers. In these experiments, **P1** was spun-coat onto glass slides and irradiated with polarized UV-light (see Supporting Information for full details). LC cells were fabricated and loaded with a small quantity of MLC-6884.<sup>13</sup> To evaluate the alignment the test cells were heated to the clearing point, slowly cooled to the nematic phase and then analyzed using a polarizing microscope. As shown in Figure 6, the non-irradiated cell does not exhibit any alignment. This is evinced by the fact that there is no apparent alignment in the schlieren textures and rotation by 45° does not elicit any changes in intensity the transmission of light through the cell. In stark contrast, the irradiated cell viewed under cross polarization displays a uniform alignment, without a schlieren texture, that displays extinction when one of the polarizers is aligned with the direction of the photolysis. The cell becomes bright when the direction cell is turned to have its polarized axis at 45° to the crossed polarizers of the microscope.



**Figure 6.** Polarized optical micrographs of LC cells containing MLC-6884 and thin-films of **P1**. The upper images correspond to the non-irradiated control cell and the bottom images correspond to cells that have been irradiated by polarized UV light.

In summary, we have shown that the di- $\pi$ -methane rearrangement is an effective approach towards the photoalignment of LC phases. The reaction is clean and highly regioselective at both the small molecule and polymer scales. We postulate that the alignment results from the minimization of IFV via the interaction of unreacted **P1** dibenzobarrelene moieties and rigid rod nematogens. Further work is currently underway to explore this concept in greater detail.

## ASSOCIATED CONTENT

### Supporting Information

Synthetic, photolysis and device fabrication details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

Timothy M. Swager, [tswager@mit.edu](mailto:tswager@mit.edu)

### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

This work was supported by the National Science Foundation DMR-1005810 and Army Research Office through the Institute for Soldier Nanotechnologies (W911NF-07-D-004).

## REFERENCES

- (a) Kim, K.-H.; Song, J.-K. *NPG Asia Mater.* **2009**, *1*, 29. (b) Semenza, P. *Inf. Disp.* **2009**, *25*, 22. (c) Lee, K. H.; Kim, H. Y.; Park, K. H.; Jang, S. J.; Park, I. C.; Lee, J. Y. *Dig. Tech. Pap. – Soc. Inf. Disp. Int. Symp.* **2006**, *37*, 1079.
- Schadt, M.; Helfrich, W. *Appl. Phys. Lett.* **1971**, *18*, 127.
- Kawatsuki, N. *Chem. Lett.* **2011**, *40*, 548.
- Yaroshchuk, O.; Reznikov, Y. *J. Mater. Chem.* **2012**, *22*, 286.
- The examples are too numerous to list. For representative examples on the topic, please see the following and references cited therein: (a) Chigrinov, V. G.; Kozenkov, V. M.; Kwok, H. S. *Photoalignment of Liquid Crystalline Materials: Physics and Applications*; John Wiley & Sons: England, 2008. (b) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.
- Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183.
- For reviews on the topic see the following: (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

(8) (a) Long, T. M.; Swager, T. M. *Adv. Mater.* **2001**, *13*, 601. (b) Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 3826. (c) Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 9670.  
(9) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 6096. (b) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4191.  
(10) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991.

(11) (a) Dorman, G.; Prestwich, G. D. *Biochemistry*, **1994**, *33*, 5661. (b) Christensen, S. K.; Chiappelli, M. C.; Hayward, R. C. *Macromolecules*, **2012**, *45*, 5237.  
(12) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605.  
(13) MLC-6884 is negative dielectric anisotropic nematic LC mixture produced by Merck KGaA.



