Photoalignment Layers for Liquid Crystals from the Di-π-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

ABSTRACT: Photoalignment of nematic liquid crystals is demonstrated using a di-π-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. 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 regiospecific, and thin films showed alignment.

Figure 1. Photochemical behavior of dibenzobarrelene substrates[6] under direct and sensitized irradiation conditions (top). Polymeric di-π-methane rearrangement of **P1** facilitated by intrapolymer triplet sensitization (bottom).

Devices that exploit the unique opto-electronic and self-assembling characteristics of liquid crystalline (LC) materials are a cornerstone of modern technology.[1] 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.[2] 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[3] and static charge at the interface of the substrate, is not compatible with surfaces with complex topographies, and can damage sensitive electronic components that are part of integrated devices.[4] To overcome this problem, noncontact alignment methods have been developed, the majority of which employ axis-selective photochemical transformations, to generate highly aligned LC phases.[4,5] 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-π-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**).[6] To address the need for new, efficient transformations that can create alignment layers, we report here the application of the di-π-methane rearrangement to create films capable of alignment of nematic liquid crystals.

Zimmerman and co-workers described the di-π-methane rearrangement in full detail, yielding predictive measures for the determination of regioselectivity and the role of excited-state multiplicity in the reaction mechanism.[7] These seminal works
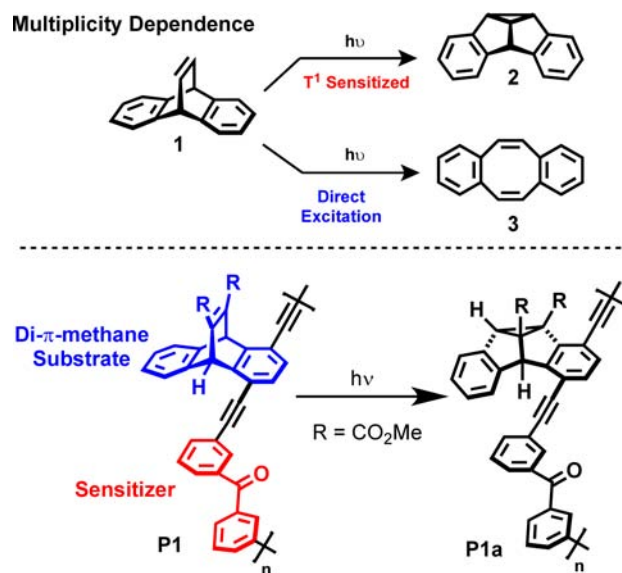
serve as a starting point for the design of a polymer capable of undergoing a regioselective di-π-methane rearrangement. Drawing upon the ability of triptycene structures to enhance the alignment of LC molecules through the minimization of internal free volume (IFV),[8] we envisioned that substituted 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.

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**.[9] 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,[10] and (2) once sensitization of the di-π-methane substrate is complete, newly formed benzophenone diradicals[11] can cross-link the film, thereby
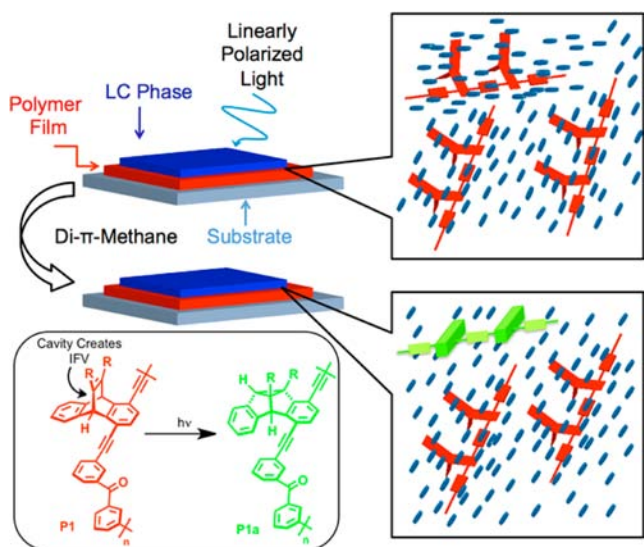
Figure 2. Schematic depiction of proposed photoalignment mechanism: red/green barbed structures, **P1/P1a**; blue ellipsoids, LC molecules.

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

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 photoisomerization.

Our proposed photoalignment is schematically depicted in Figure 2 and operates as follows: (1) selective excitation of benzophenone units by polarized light 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 though 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 ethynylenes) (PPEs).[12] 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 of 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
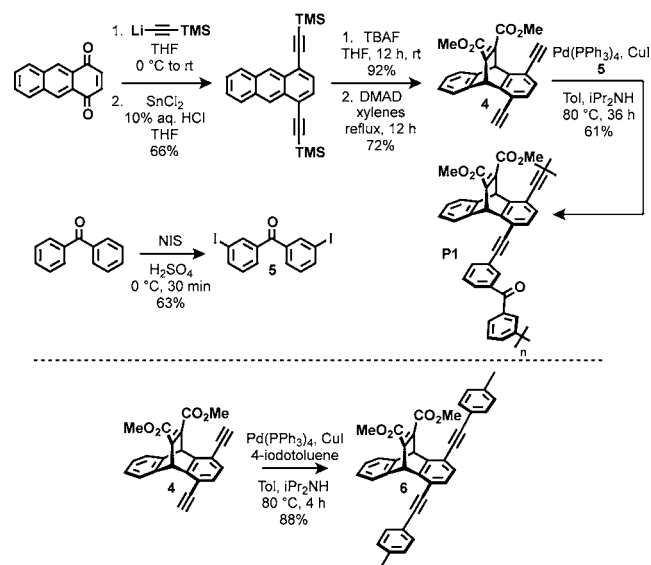
substituted barrelene scaffolds—such substrates could potentially yield two racemic photoproducts (Figure 3).
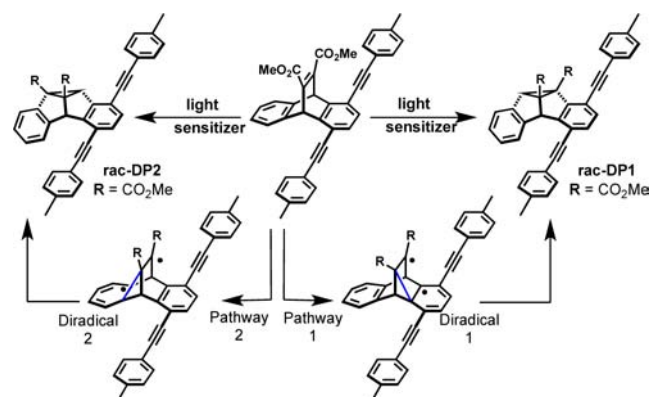
Figure 3. Postulated photochemical pathways available to model compound **6** after sensitized excitation.

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 ¹H 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 selectively 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
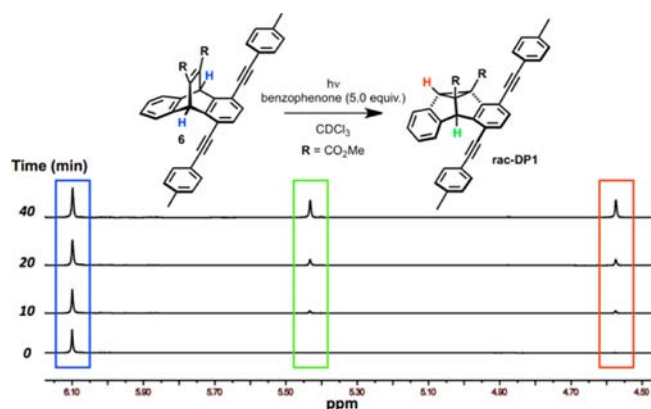
Figure 4. Di-π-methane rearrangement of model compound **6** (top). Time-elapsed ^{1}H NMR spectra recorded during the sensitized photolysis of **6** (bottom). The intensity is normalized to the resonance at 6.1 ppm, and the signals in the blue, green, and red boxes are assigned to the protons colored similarly in the structures.

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, projecting in a fashion that can block interactions between liquid crystal molecules and the plane created by the rigid phenylethynyl 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.

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
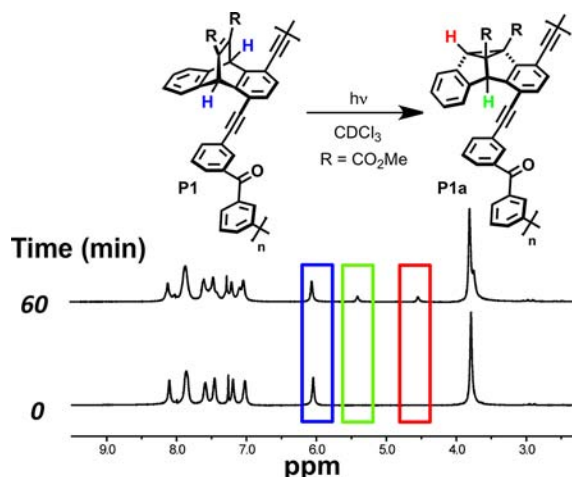
Figure 5. Di-π-methane rearrangement of **P1** (top). Time-elapsed ^{1}H NMR spectra of the reaction (bottom). The signals in the blue, green, and red boxes are assigned to the protons colored similarly in the structures.

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 toward the fabrication of LC alignment layers. In these experiments, **P1** was spun-coated 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.[13] 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,
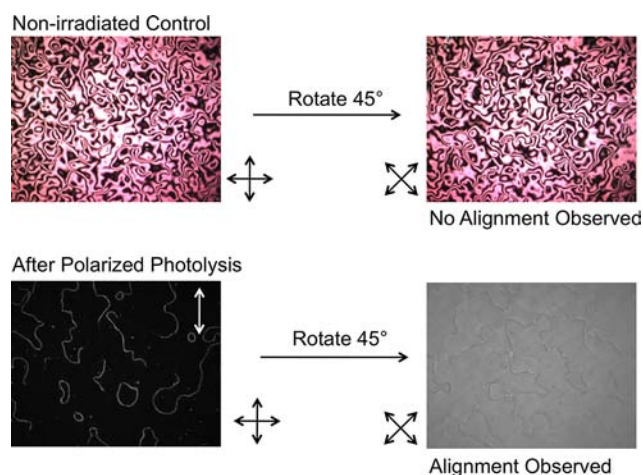
Figure 6. Polarized optical micrographs of LC cells containing MLC-6884 and thin films of **P1**. The upper images correspond to the non-irradiated control cell, and the bottom images correspond to cells that have been irradiated by polarized UV light.

the non-irradiated cell does not exhibit any alignment. This is evidenced by the fact that there is no apparent alignment in the schlieren textures, and rotation by 45° does not elicit any changes in intensity in 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 polarization of the photolysis. The cell becomes bright when the cell direction is turned so that its alignment axis is oriented at 45° to the crossed polarizers of the microscope.

In summary, we have shown that the di-π-methane rearrangement is an effective approach toward 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
Details of synthesis, photolysis, and device fabrication. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
tswager@mit.edu

Notes

The authors declare no competing financial interest.

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dx.doi.org/10.1021/ja312090p | *J. Am. Chem. Soc.* 2013, 135, 640−643