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Enabling Lower Energy Light Harvesting in Stilbene-Based Photomechanical Polymers via Triplet Sensitization

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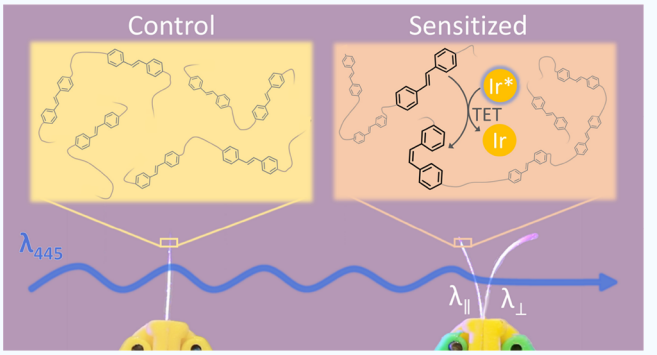
ABSTRACT: Photoresponsive polymers, typically activated with direct excitation of an azobenzene moiety, are an intriguing class of materials for application as adaptive structures. Here, we introduce triplet excited state sensitization as a mechanism to harness light in a stilbene-based photopolymer (i.e., the carbon analogue of azobenzene). While the undoped film shows no response, the sensitized film exhibits polarization dependent bending under 445 nm irradiation via (1) sensitizer excitation, (2) triplet energy transfer, (3) stilbene isomerization, and (4) subunit reorientation. This work is the first to demonstrate stilbene-based photopolymers and triplet sensitization as a low energy light harvesting mechanism in photomechanics.



KEYWORDS: *actuators, composite materials, polyimides, photoisomerization, triplet sensitization, stilbene*

Stimuli-responsive materials are important for a broad range of adaptive structure applications including in robotics, aerospace engineering, drug delivery, and heliostats.[1] Piezoelectric ceramics, magnetostrictive materials, and shape memory alloys are well-known for their use in such applications.[1] Photoresponsive polymers are another intriguing class of adaptive materials that exhibit spatial and temporal shape changes dictated by the location and intensity of irradiation.[1−3] Consequently the polymer material can be controlled using a remote source, like a laser, without the need for a tethered electric circuit or power supply. Unfortunately the conversion of light into mechanical work is often energetically inefficient and only small amounts of mechanical force are generated.[1,3]

The vast majority of photomechanical polymers rely on light absorption and structural change of azobenzene molecules/subunits.[2,4−9] That is, under UV (<400 nm) and deep-blue light (400−450 nm), azobenzene undergoes a well-known *trans*-to-*cis* and *cis*-to-*trans* isomerization, respectively.[10] When embedded and/or incorporated into a polymer matrix, anisotropic *trans*−*cis*−*trans* photoisomerization translates to a bulk mechanical response from the polymer film.

Stilbene (highlighted in blue in Figure 1a), the carbon-based analogue of azobenzene, can also undergo photoinduced *trans*−*cis*−*trans* isomerization.[11] Yet, despite having a higher activation barrier for isomerization and the potential to increase the amount of mechanical force, there are no reports of stilbene-based polymers being used as photomechanical films to date. Presumably, this is at least partly due to the significantly hypsochromically shifted absorption of stilbene relative to azobenzene, thus requiring UV light to directly generate the singlet excited state and elicit a response. The need for UV light fundamentally limits any potential utility of a stilbene photopolymer because it requires expensive LEDs/lasers, the solar spectrum includes small UV contribution, and the high energy of UV light can damage both the chromophore and the polymer backbone.

While UV light is necessary for isomerization via the singlet excited state (S_1), stilbene has long been known to isomerize via the much lower energy triplet excited state (T_1) manifold.[12−14] While the ground to triplet excited state transition ($S_0 \rightarrow T_1$) is typically forbidden, the T_1 state can readily be accessed through energy transfer from a triplet sensitizer. Incorporating such a scheme into a photomechanical polymer could enable the use of lower energy light, increase the depth of light penetration, and decrease photodegradation of the film. Here, we demonstrate that the incorporation of an iridium(III) cyclometalated sensitizer into a stilbene-polyimide based film enables (1) the harnessing of lower energy light (445 nm), (2) triplet energy transfer (TET) from the sensitizer to stilbene, (3) isomerization of stilbene via

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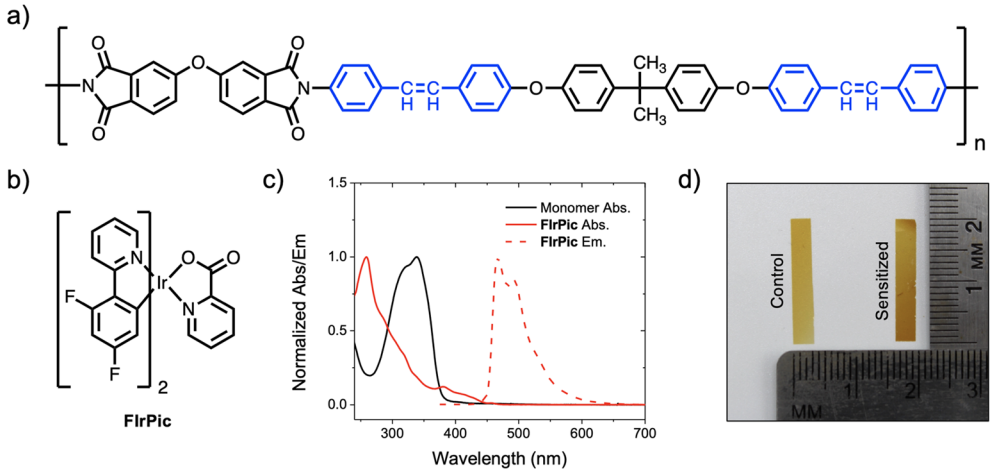

Figure 1. Structures of (a) the stilbene functionalized polymer with the stilbene moiety highlighted in blue and (b) the iridium(III)bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato) sensitizer (**FIrPic**). (c) Normalized absorbance and emission spectra for the stilbene monomer and **FIrPic** sensitizer in DCM and (d) pictures of polymer films both without (control) and with (sensitized) **FIrPic** doping.

the triplet excited state, and (4) a photomechanical response from the polymer films. Particularly notable is that the direction of film bending can be controlled with the polarization of incident light indicating that anisotropic excited states are retained through the sensitization mechanism. This behavior strongly suggests *trans*−*cis*−*trans* photoisomerization in comparison to the more widely observed *trans*−*cis* photoisomerization process.[15]

The stilbene-based polyimide polymer and iridium sensitizer studied here are shown in Figure 1a,b with the absorption and emission spectra in Figure 1c. This polymer was targeted because it is the stilbene analogue of a known azobenzene polyimide photomechanical polymer.[7] The sensitizer molecule, iridium(III)bis[2-(4,6-difluorophenyl)pyridinato-C2,N]-(picolinato), herein referred to as **FIrPic**, was selected because (1) it is commercially available, (2) it has absorption features that extend into the visible region (Figure 1c), (3) iridium cyclometalated complexes are known to undergo fast intersystem crossing with an ∼100% triplet yield, and (4) its triplet energy (2.65 eV)[16] is sufficiently high to favor TET to stilbene (2.14 eV)[17] as shown in Figure 2.

The stilbene monomer, 4,4′-((propane-2,2-diylbis(4,1-phenylene)bis(oxy)bis(4,1-phenylene))bis(ethylene-2,1-diyl))dianiline, was synthesized in three steps with an overall

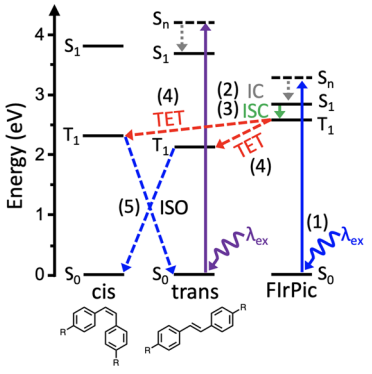

Figure 2. Energy diagram and dynamic events for a polymer film containing stilbene monomer and **FIrPic** sensitizer (IC = internal conversion, ISC = intersystem crossing, TET = triplet energy transfer, ISO = isomerization).

15.6% yield.[18−20] The polymer film was then prepared using an imide coupling reaction following a previously published procedure.[7] Briefly, 4,4′-oxidiphthalic anhydride was added to a dimethylacetamide solution containing the stilbene monomer and left to stir for 24 h. The viscous solution was then diluted and poured onto a glass slide and heated under vacuum at 50 °C for 1 h to remove the solvent before thermal imidization at 250 °C. ATR-FTIR spectra of the diamine and dianhydride monomers as well as the film after thermal imidization are shown in Figure S5. The disappearance of the N−H stretch of the amine at 3500−3300 cm^{-1} and C═O stretch of the anhydride at 1845 cm^{-1} as well as the appearance of a C═O stretch of bismaleimide at 1710 cm^{-1} are consistent with the formation of imide bonds.[21] Attempts to determine the degree of polymerization (i.e., the molar mass) by NMR and SEC were unsuccessful due to the insoluble nature of the resulting film in all solvents tested (e.g., THF, DMF, DMSO). The absence of key signals in ATR-FTIR that correspond to unreacted amine or anhydride functionalities (Figure S5) in the films suggest that the extent of reaction is high. While we are unable to quantify the degree of polymerization, a high extent of reaction indicates that at least modest molar mass has been achieved (i.e., Carothers equation) and that a negligible amount of monomers remain.[22] The films containing the sensitizer molecule were prepared following a similar procedure but with the addition of 10 mol % of **FIrPic** into the solution. The ATR-FTIR spectra were similar for both the sensitized and unsensitized films (Figure S5).

It is worth noting that we made no attempts to vary or optimize the **FIrPic** doping concentration for these proof-of-concept films. Such efforts will require balancing the depth of light penetration, fraction of the stilbene within the TET radius, and the film thickness to elicit a desired response (i.e., film bending vs constriction). Additional synthetic details are provided in the Supporting Information.

Both the sensitized and unsensitized films exhibited a similar thickness (∼25 μm; Table S1), and only an ∼20 °C difference in the decomposition ($T_{d(unsen)}$ = 380 °C; $T_{d(sen)}$ = 360 °C) and glass transition ($T_{g(unsen)}$ = 210 °C; $T_{g(sen)}$ = 187 °C) temperatures (Figures S6 and S7 and Table S1). Although the ATR-FTIR spectra of the sensitized and unsensitized films are similar (Figure S5), we are unable to quantitatively determine

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the molecular weight of the polymer. Consequently, it is possible that subtle changes in the degree of polymerization may be responsible for the decrease in T_g upon addition of the sensitizer.

The addition of **FIrPic** did, however, result in a readily observable color change (Figure 1d) due to the additional 400−450 nm absorption by the sensitizer molecule as observed from the solid-state absorption spectrum (Figure S8). As an aside, in comparison to the analogous azobenzene polyimide polymer T_g (276 °C) and T_d (420 °C),[7] the stilbene polymer showed a lower T_g (210 °C) and T_d (380 °C). The origin of this difference in properties is not clear to us at this time.

The films were cut into 3 mm × 20 mm strips for photomechanical measurements. The strips were irradiated with 365 or 445 nm light, and the response was monitored via photograph/video. The results are shown in Figure 3, and additional images can be found in the Supporting Information.

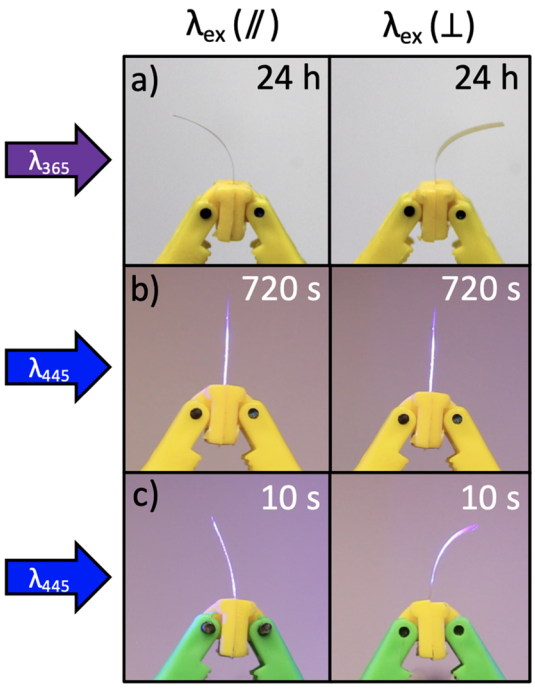

Figure 3. Photomechanical response of the control (top/middle) films under (a) 365 nm (5 mW cm^{-2}) and (b) 445 nm light (680 mW cm^{-2}) polarized either parallel (left) or perpendicular (right) to the long-axis of the film. (c) Sensitized (bottom) films under 445 nm light (680 mW cm^{-2}) polarized either parallel (left) or perpendicular (right) to the long-axis of the film.

Under vertical and horizontal 365 nm excitation (5 mW cm^{-2}), both the control and sensitized films bend toward and away from the light source, respectively (Figure 3,top). This response is similar to that observed with azobenzene photopolymers[6] and is attributed to direct excitation of stilbene and subsequent *trans*-to-*cis* and *cis*-to-*trans* isomerization from the singlet excited state manifold. The film as prepared is isotropic, but the polarized light preferentially excites the stilbene moieties with their transition moments aligned parallel to the incident light. Then, *trans*−*cis*−*trans* isomerization can occur until the stilbene moieties reorient orthogonal to the excitation source and are no longer excitable. The bulk realignment of the stilbene units results in a surface contraction or expansion of the polymer under vertically and horizontally polarized light, respectively.[6,23,24]

Performing the same experiment but under 445 nm light resulted in no change with the control sample (i.e., no sensitizer) even over 720 s of irradiation with a much more intense light source (680 mW cm^{-2}). The lack of response for the control film is not surprising given the nearly 100% transmittance (∼0 absorbance) for the stilbene moiety at 445 nm (Figure 1c). However, under 445 nm excitation, the sensitized film bent toward and away from the vertically and horizontally polarized light, respectively. In fact, a >10° displacement from their respective starting positions was achieved in only 15 s of irradiation (Figure S9). Particularly notable is that although the excitation and isomerization events occur on different species (i.e., the sensitizer and stilbene moiety, respectively), a polarization dependent response is still observed.

Thermal imaging indicates that there is a temperature increase of ∼55 °C for the sensitized film but minimal temperature change for the unsensitized film after 30 s of 445 nm irradiation (Figure S10). However, there are several indicators that thermal changes alone are not responsible for the mechanical response. First, the polarization dependent bending is analogous to the azobenzene polymers which is due to the well-known photoisomerization mechanism. Second, the process is thermally reversible where heating the films on a surface returns them to their undeformed (flat) state that repeatedly bends under additional irradiation. Third, the same polarization dependent bending was observed when the film was mounted upside down (Figure S11) indicating that the response is not due to film softening as observed when heated. Finally, the photoinduced temperature increase (55 °C) is well below the T_g of the film (187 °C), suggesting that the transition to a rubbery, more flexible phase does not occur under irradiation.

The proposed mechanism for the photoinduced film bending is depicted in Figure 2, and the steps were probed using steady-state and time-resolved spectroscopy. In the sensitized film, excitation, internal conversion, and intersystem crossing (steps 1, 2, and 3 in Figure 2) of **FIrPic** are known to occur in <500 fs.[25] TET from the triplet excited state of **FIrPic** to the stilbene moiety was investigated in solution using a Stern−Volmer analysis and the results are shown in Figure 4a and Figure S12. In this experiment, phosphorescent emission decay for **FIrPic** in solution was monitored with respect to the concentration of added stilbene monomer. The emission quenching rate constant of 5.4 × 10^9 M^{-1} s^{-1} is in agreement with a diffusion limited energy transfer event in dichloromethane (DCM).[26] No emission was observed from **FIrPic** in the polymer film suggesting that the FIrPic to stilbene subunit TET rate is at least 2 orders of magnitude faster (i.e., k_{TET} > 10^8 s^{-1}) than the intrinsic decay of **FIrPic** (τ = 1.52 μs; k_{r+nr} = 6.6 × 10^5 s^{-1}). Presumably, a rapid TET mechanism is favorable due the proximity of **FIrPic** and stilbene in the solid-state films.

The triplet sensitized *trans*-to-*cis* photoisomerization reaction (steps 4 and 5 in Figure 2) in solution was monitored using UV−vis spectroscopy, and the results are shown in Figure 4b and Figure S13. As expected, direct excitation of the stilbene monomer in DCM with 365 nm light resulted in a decrease in absorption from 280 to 375 nm and an increase in absorption from 230 to 280 nm, which is consistent with *trans*-to-*cis* isomerization of stilbene.[27] However, for a similar

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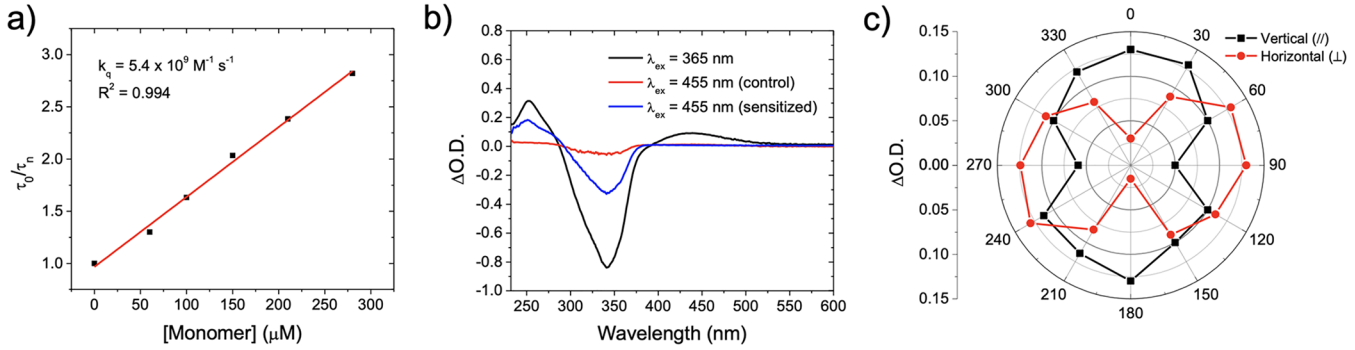

Figure 4. (a) Stern−Volmer plot for the excited state lifetime of **FIrPic** in DCM (20 μM) versus the concentration of stilbene monomer (λ_{ex} = 360 nm, λ_{em} = 466 nm) and (b) change in UV−vis absorbance of the stilbene monomer (50 μM) in DCM after 5 min of irradiation with and without 5.0 μM **FIrPic**. (c) Polar absorption plot depicting the difference in absorption at 445 nm for the sensitized polymer films before and after irradiation with 445 nm (50 mW cm^{-2}) for 60 min (angle reported relative to the long axis of the film).

solution under 455 nm excitation, no spectral change was observed due to a lack of absorption by stilbene. In contrast, 455 nm excitation of the solution containing stilbene monomer and 10 mol % **FIrPic** results in similar spectra changes as with direct excitation of the monomer. Given that **FIrPic** is a known triplet sensitizer[28,29] and 455 nm (2.72 eV) light is well below the stilbene singlet excited state energy (3.3 eV), these observations further support **FIrPic** to stilbene TET followed by a *trans*-to-*cis* isomerization reaction from the triplet excited state manifold of stilbene.

As noted above, the sensitized film exhibits a polarization dependent response suggesting that excitation, TET, and isomerization are anisotropic processes. One common means of probing the films polarization dependence is via polarized UV−vis absorption measurements. For this measurement, the polarized absorption of the sensitized films was measured before and after irradiation with vertically and horizontally polarized 445 nm light (Figures S14−S17). This data is typically plotted in raw absorption units[6] but here, due to the competitive absorption of **FIrPic** and stilbene, delta absorbance (ΔO.D.) was used and the results are shown in Figure 4c. The absorption for the as prepared polymer film is the same in all directions. However, following irradiation with polarized 445 nm light, the films exhibit the largest ΔO.D. along the axis of excitation. That is, vertical excitation induced the largest ΔO.D. at 0° and 180° and at 90° and 270° for perpendicular excitation. The observation of a change in polarized absorption but unperturbed isotropic absorption, in combination with the bidirectional bending of the film upon polarized excitation, support an anisotropic TET event followed by *trans*−*cis*−*trans* isomerization and realignment of the stilbene subunits.[30] Orientation dependent TET is not that surprising given the orbital overlap that is required for Dexter energy transfer to occur.[31] Interestingly, as far as we can tell, the absorption of **FIrPic** remains isotropic after irradiation. This observation suggests that either (1) that **FIrPic** is free to rotate but TET occurs much faster than rotation, or more likely (2) the **FIrPic** molecules are immobile due to the glassy nature of the film below the T_g, and thus, polarization during TET is retained.

In summary, a stilbene-based polyimide polymer film has been synthesized and doped with an iridium(III) cyclometalated triplet sensitizer molecule (**FIrPic**). In contrast to the unsensitized film that is unperturbed under 445 nm irradiation, the sensitized film exhibits a polarization dependent photomechanical response. More specifically, the film bends toward and away from the vertically and horizontally polarized light source, respectively. Spectroscopic measurements support a stepwise mechanism involving (1) excitation of **FIrPic** sensitizers followed by internal conversion and intersystem crossing to the triplet excited state, (2) triplet energy transfer from **FIrPic** to the stilbene subunit, (3) *trans*−*cis*−*trans* isomerization from the triplet excited state of stilbene, and (4) reorientation of the stilbene subunit resulting in a bulk contraction or expansion at the surface of the film. Particularly notable is that although the excitation and isomerization events occur on different species, a polarization dependent response is still observed indicating that anisotropic excited states are retained through the triplet energy transfer event. Collectively, these results are notable in that this is the first demonstration of a stilbene-based photomechanical polymer and that the low energy triplet of stilbene can be utilized to elicit a mechanical response. More broadly, this work demonstrates that triplet sensitization can serve as a new, low energy light harvesting mechanism in photomechanical polymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.2c00660.

Synthetic details, ATR-FTIR spectra, TGA, DSC, bending photos, Stern−Volmer data, and additional absorption spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kundys, B. Photostrictive materials. *Appl. Phys. Rev.* **2015**, *2* (1), No. 011301.

(2) Barrett, C. J.; Mamiya, J.-i.; Yager, K. G.; Ikeda, T. Photo-mechanical effects in azobenzene-containing soft materials. *Soft Matter* **2007**, *3* (10), 1249−1261.

(3) Kondo, M. Photomechanical materials driven by photo-isomerization or photodimerization. *Polym. J.* **2020**, *52* (9), 1027−1034.

(4) White, T. J.; Serak, S. V.; Tabiryan, N. V.; Vaia, R. A.; Bunning, T. J. Polarization-controlled, photodriven bending in monodomain liquid crystal elastomer cantilevers. *J. Mater. Chem.* **2009**, *19* (8), 1080−1085.

(5) Wang, D. H.; Lee, K. M.; Yu, Z.; Koerner, H.; Vaia, R. A.; White, T. J.; Tan, L.-S. Photomechanical Response of Glassy Azobenzene Polyimide Networks. *Macromolecules* **2011**, *44* (10), 3840−3846.

(6) Lee, K. M.; Tabiryan, N. V.; Bunning, T. J.; White, T. J. Photomechanical mechanism and structure-property considerations in the generation of photomechanical work in glassy, azobenzene liquid crystal polymer networks. *J. Mater. Chem.* **2012**, *22* (2), 691−698.

(7) Wang, D. H.; Wie, J. J.; Lee, K. M.; White, T. J.; Tan, L.-S. Impact of Backbone Rigidity on the Photomechanical Response of Glassy, Azobenzene-Functionalized Polyimides. *Macromolecules* **2014**, *47* (2), 659−667.

(8) Xue, C.; Xiang, J.; Nemati, H.; Bisoyi, H. K.; Gutierrez-Cuevas, K.; Wang, L.; Gao, M.; Zhou, S.; Yang, D.-k.; Lavrentovich, O. D.; Urbas, A.; Li, Q. Light-Driven Reversible Alignment Switching of Liquid Crystals Enabled by Azo Thiol Grafted Gold Nanoparticles. *ChemPhysChem* **2015**, *16* (9), 1852−1856.

(9) Chen, H.; Chen, W.; Lin, Y.; Xie, Y.; Liu, S. H.; Yin, J. Visible and near-infrared light activated azo dyes. *Chin. Chem. Lett.* **2021**, *32* (8), 2359−2368.

(10) Ikeda, T.; Sasaki, T.; Ichimura, K. Photochemical switching of polarization in ferroelectric liquid-crystal films. *Nature* **1993**, *361* (6411), 428−430.

(11) Waldeck, D. H. Photoisomerization dynamics of stilbenes. *Chem. Rev.* **1991**, *91* (3), 415−436.

(12) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. Mechanisms of Photochemical Reactions in Solution. XXII.1 Photochemical cis-trans Isomerization. *J. Am. Chem. Soc.* **1964**, *86* (16), 3197−3217.

(13) Saltiel, J.; Chang, D. W. L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. The triplet state in stilbene cis-trans photoisomerization. *Pure Appl. Chem.* **1975**, *41* (4), 559−579.

(14) Orlandi, G.; Monti, S.; Barigelletti, F.; Balzani, V. Triplet energy transfer to cis and trans stilbene. A quantum mechanical approach. *Chem. Phys.* **1980**, *52* (3), 313−319.

(15) Wang, H.; Lee, K. M.; White, T. J.; Oates, W. S. trans−cis and trans−cis−trans Microstructure Evolution of Azobenzene Liquid-Crystal Polymer Networks. *Macromol. Theory Simul.* **2012**, *21* (5), 285−301.

(16) Zhang, L.; Li, X.-L.; Luo, D.; Xiao, P.; Xiao, W.; Song, Y.; Ang, Q.; Liu, B. Strategies to Achieve High-Performance White Organic Light-Emitting Diodes. *Materials* **2017**, *10* (12), 1378.

(17) Neveselý, T.; Wienhold, M.; Molloy, J. J.; Gilmour, R. Advances in the E → Z Isomerization of Alkenes Using Small Molecule Photocatalysts. *Chem. Rev.* **2022**, *122* (2), 2650−2694.

(18) Das, R. K.; Saha, B.; Rahaman, S. M. W.; Bera, J. K. Bimetallic Catalysis Involving Dipalladium(I) and Diruthenium(I) Complexes. *Chem.—Eur. J.* **2010**, *16* (48), 14459−14468.

(19) Bizier, N. P.; Wackerly, J. W.; Braunstein, E. D.; Zhang, M.; Nodder, S. T.; Carlin, S. M.; Katz, J. L. An Alternative Role for Acetylenes: Activation of Fluorobenzenes toward Nucleophilic Aromatic Substitution. *J. Org. Chem.* **2013**, *78* (12), 5987−5998.

(20) Hahm, S. G.; Lee, S. W.; Lee, T. J.; Cho, S. A.; Chae, B.; Jung, Y. M.; Kim, S. B.; Ree, M. UV-Driven Switching of Chain Orientation and Liquid Crystal Alignment in Nanoscale Thin Films of a Novel Polyimide Bearing Stilbene Moieties in the Backbone. *J. Phys. Chem. B* **2008**, *112* (16), 4900−4912.

(21) Hasegawa, M.; Fujii, M.; Wada, Y. Approaches to improve the film ductility of colorless cycloaliphatic polyimides. *Polym. Adv. Technol.* **2018**, *29* (2), 921−933.

(22) Lodge, T.; Hiemenz, P. C. *Polymer Chemistry*; CRC Press, 2020.

(23) Sekkat, Z.; Wood, J.; Knoll, W.; Volksen, W.; Miller, R. D.; Knoesen, A. Light-induced orientation in azo-polyimide polymers 325 °C below the glass transition temperature. *J. Opt. Soc. Am. B* **1997**, *14* (4), 829−833.

(24) Sekkat, Z.; Wood, J.; Aust, E. F.; Knoll, W.; Volksen, W.; Miller, R. D. Light-induced orientation in a high glass transition temperature polyimide with polar azo dyes in the side chain. *J. Opt. Soc. Am. B* **1996**, *13* (8), 1713−1724.

(25) Duan, H.-S.; Chou, P.-T.; Hsu, C.-C.; Hung, J.-Y.; Chi, Y. Photophysics of Heteroleptic Iridium(III) Complexes Of Current Interest; a Closer Look on Relaxation Dynamics. *Inorg. Chem.* **2009**, *48* (14), 6501−6508.

(26) Yu, D. H. S.; Torkelson, J. M. Diffusion-limited phosphorescence quenching interactions in polymer solutions: small molecule-small molecule interactions interpreted by free volume theory. *Macromolecules* **1988**, *21* (4), 1033−1041.

(27) Sumitani, M.; Yoshihara, K. Direct Observation of the Rate for Cis→Trans and Trans→Cis Photoisomerization of Stilbene with Picosecond Laser Photolysis. *Bull. Chem. Soc. Jpn.* **1982**, *55* (1), 85−89.
(28) Jiang, Y.; Lv, P.; Pan, J.-Q.; Li, Y.; Lin, H.; Zhang, X.-W.; Wang, J.; Liu, Y.-Y.; Wei, Q.; Xing, G.-C.; Lai, W.-Y.; Huang, W. Low-Threshold Organic Semiconductor Lasers with the Aid of Phosphorescent Ir(III) Complexes as Triplet Sensitizers. *Adv. Funct. Mater.* **2019**, *29* (19), 1806719.
(29) Dey, A.; Kabra, D. Kinetics of Triplet Exciton Energy-Transfer Processes in Triplet Sensitizer-Doped Fluorescent Polymers. *J. Phys. Chem. A* **2019**, *123* (23), 4858−4862.
(30) Wang, H.; Lee, K. M.; White, T. J.; Oates, W. S. trans−cis and trans−cis−trans Microstructure Evolution of Azobenzene Liquid-Crystal Polymer Networks. *Macromol. Theory Simul.* **2012**, *21* (5), 285−301.
(31) Dexter, D. L. A Theory of Sensitized Luminescence in Solids. *J. Chem. Phys.* **1953**, *21* (5), 836−850.

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