

Three-Dimensional Photo-Cross-Linkers for Nondestructive Photopatterning of Electronic Materials

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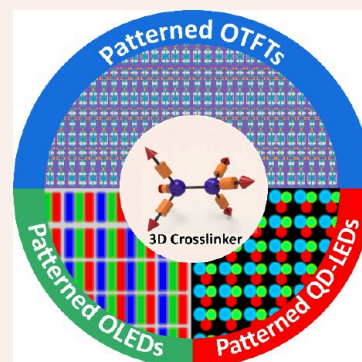
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CONSPECTUS: Solution-processed electronics have shown promise in cost-effective manufacturing, but face challenges in precisely and accurately placing electronic materials. Traditional methods, such as photolithography with photoresists, involve complex steps that can damage electronic materials. Alternatives such as orthogonal patterning and inkjet printing are limited by the difficulty of finding compatible chemicals that do not dissolve underlying layers, while nanoimprinting lacks compatibility with high-throughput processes and suffers from poor chemical robustness. Conventional photo-cross-linking approaches have used organic or polymeric agents to pattern electronic layers, but the consecutive application of photo-cross-linking processes for patterning and stacking of multiple electronic materials typically led to degradation of the intrinsic properties of the materials.

To overcome these issues, we have demonstrated a promising photopatterning strategy of using highly efficient, three-dimensional photo-cross-linkers bearing multiple phenyl azides. Specifically, electronic materials hosting a minimal amount of the photo-cross-linkers were photo-cross-linked under UV through a photomask, followed by subsequent removal of the uncross-linked parts using a developing solvent. This method produces a patterned electronic layer that maintains chemical and physical stability while enhancing the thermal and mechanical stabilities. The successive patterning of electronic materials in this approach has precise control over parallel or vertical stacking of high-resolution electronic material layers without optical/electrical property loss. This Account provides an overview of our efforts toward photopatterning electronic materials in the field of polymer thin film transistors (PTFTs), organic light-emitting diodes (OLEDs), and quantum-dot light-emitting diodes (QD-LEDs). First, two azide-based multibridged photo-cross-linkers (i.e., 4Bx and 6Bx) were developed and applied to fabricate all-solution-processed PTFTs. These cross-linkers have excellent cross-linkability compared to a conventional bifunctional photo-cross-linker (i.e., 2Bx), leading to fabricating thin-film electronic layer patterns and acquiring chemical resistance of each layer. Moreover, they effectively reduce leakage current and enhance the electrical strength in dielectric layers. This research underscores the crucial role of efficient cross-linkers in achieving all-solution-processed, all-photopatterned organic electronic devices while preserving their intrinsic electrical properties of employed semiconducting polymers. These cross-linkers have also been applied for OLEDs, which produces high-resolution photopatterned light-emitting polymer semiconductors. Furthermore, azide-based photo-cross-linking chemistry has been applied to the patterning of luminescent QDs. A breakthrough approach of utilizing a bulky isopropyl group-containing photo-cross-linker (i.e., IP-6-LiXer) has been demonstrated to form high-fidelity patterns of heavy-metal-free QDs to realize high-resolution full-color QD-LEDs. IP-6-LiXer allows efficient photo-cross-linking between QDs without harming the optical/electrical properties of QDs. The six azide groups at its terminals cross-link the QDs by forming covalent bonds selectively with the ligands on the QD surfaces. The isopropyl groups in IP-6-LiXer inhibit the undesirable chemical contact between azide groups and core metals in the QDs. This characteristic of these cross-linkers leads to nondestructive direct photopatterning of luminescent heavy-metal-free QDs. Lastly, we conclude that our approaches have been effective across various electronic materials, including polymers and QDs, emphasizing the versatility and potentials in the various optoelectronic devices.



1. INTRODUCTION

Solution-processed electronics have great potential to revolutionize future electronics due to their cost-effectiveness, flexibility, and light weight.^{1–4} However, fabricating devices entirely through solution-processes is quite difficult because solution-cast electronic layers are easily formed but can also be easily erased or damaged by the following solution processes unless they are not post-treated or an orthogonal solvent is used for the follow-up solution-processing. Thus, precise patterning and stacking of multiple electronic components remains still

challenging. Specifically, conventional photolithography is a representative method to produce high-resolution patterns, but

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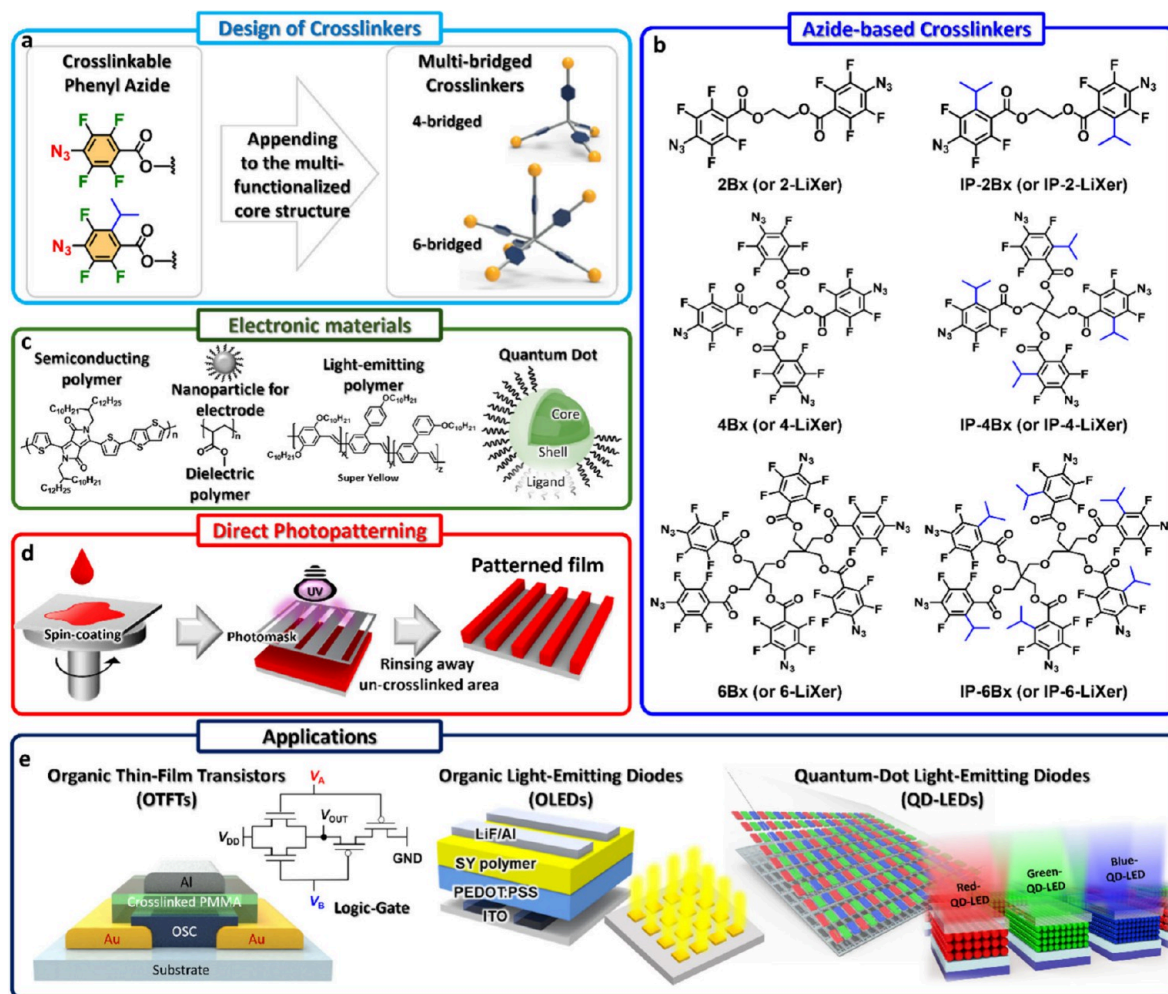


Figure 1. (a) The chemical design of azide-based n -bridged photo-cross-linkers and (b) synthesized azide-based cross-linkers. (c) Potentially cross-linkable electronic materials. (d) Direct photopatterning process composed of (i) spin-coating of photo-cross-linker containing target material solution, (ii) photo-cross-linking under UV, and (iii) developing with a mother solvent. (e) Examples of applicable electronic devices.

faces limitations in that it needs many complicated steps and the process of an overlying layer often degrades the optical and electrical properties of pre-coated underlying layers through chemical and physical damages when creating solution-processable materials.^{5,6} Alternatively, inkjet printing and nanoimprinting methods have been developing due to their simplicity in forming electronic layers, but they also have difficulties in achieving high film uniformity, stacked multilayers, and scalability.^{7,8} In this regard, direct photopatterning of target materials using a photo-cross-linking agent and a photomask can be an attractive approach to enable selective and chemically intact patterning as long as the photo-cross-linking process does not affect their optical and electrical properties (Figure 1). Among reported photo-cross-linkers,⁹ those containing azide ($-N_3$) groups are of particular interest because of their unique features, including:

- Compatibility with a wide range of materials, including polymers, small molecules, nanoparticles, and hybrid materials, which offers versatility in patterning diverse electronic materials.
- Precise control over the dimensions, shape, and positioning of patterned layers, which allows high-resolution patterning.

- Facile application into scalable manufacturing processes such as inkjet printing or roll-to-roll printing, which facilitates large-scale production of patterned electronic devices.
- Rapid and efficient photo-cross-linkability under UV light with enhanced thermal and mechanical properties.
- Little detrimental effects on the optical/electrical properties of the semiconducting materials without generation of harmful side products when they are incorporated in a carefully designed chemical structure.

Azide-based photo-cross-linkable agents include azide-containing polymers,^{10,11} azide-modified small molecules,¹² and azide-functionalized nanoparticles.¹³ The azide group can make photoinduced reaction with suitable reactive partners, such as alkyl chains, upon exposure to UV light. Under UV light, photolysis of the azide group results in the formation of singlet nitrene.¹⁴ Singlet nitrene is highly reactive and relevant for effective cross-linking via C–H insertion reaction. It should also be noted that singlet nitrene has a limited lifetime and can turn into triplet nitrene which behaves as a diradical and leads to ring expansion, dimerization, or side reactions that do not trigger cross-linking.¹⁵ Compared to alkyl nitrenes (the product of alkyl azides), phenyl nitrenes (the product of phenyl azides) are chemically more stable and undergo C–H insertion more

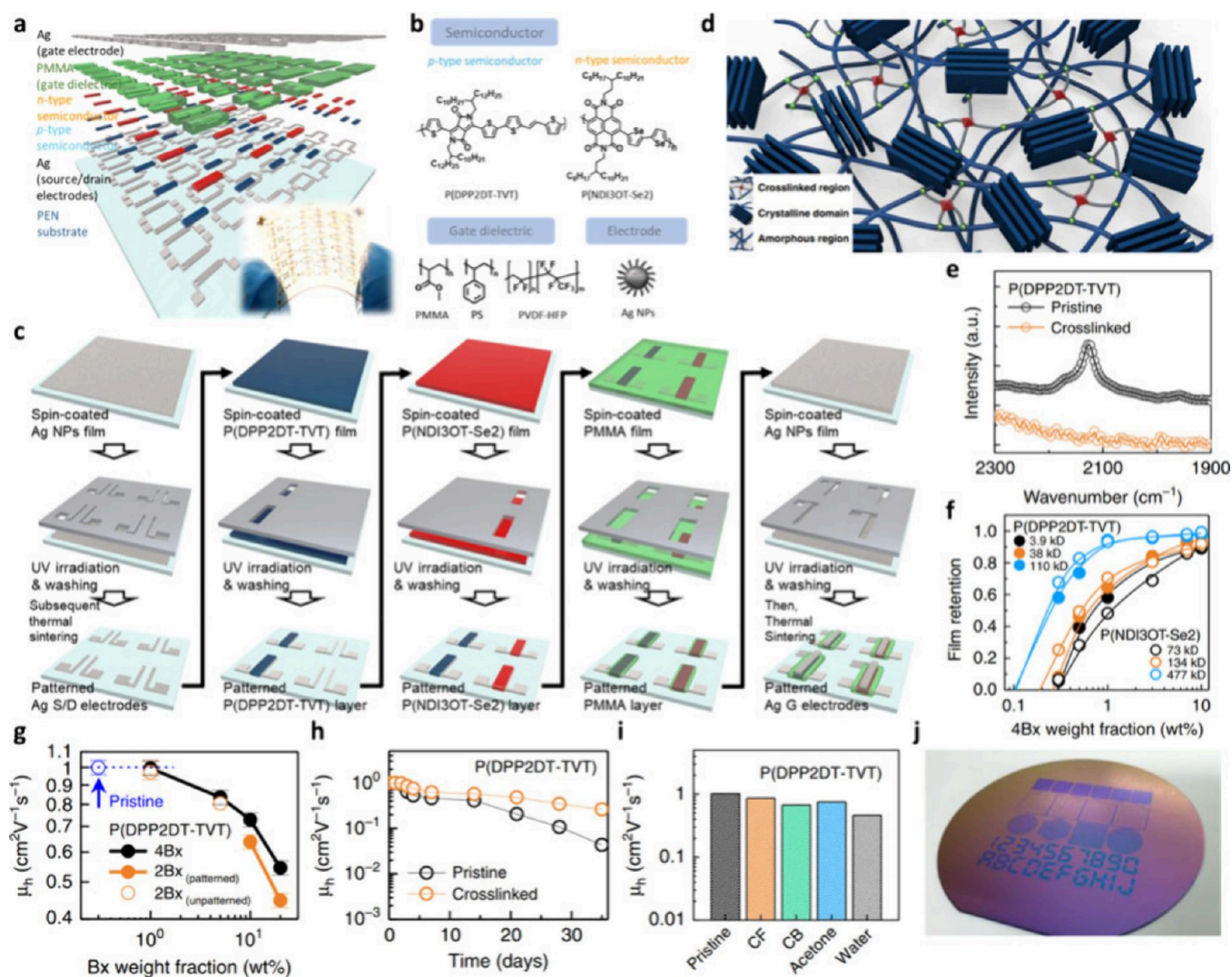


Figure 2. (a) A schematic representation and photographic image of fully photopatterned PTFTs and logic circuits on a plastic substrate, created by patterning semiconducting channels, gate dielectrics, and electrode materials. (b) Chemical structures of the electronic materials used in the study. (c) A schematic outlining the fabrication steps for p- and n-type PTFTs using all-photopatterning with 4Bx. (d) Diagram illustrating the cross-linked state of a semiconducting polymer formed with 4Bx. (e) FTIR spectra of P(DPP2DT-TVT) films before and after cross-linking. (f) Film retention properties of P(DPP2DT-TVT) and P(NDI3OT-Se2) at varying 4Bx content. (g) Hole mobilities of PTFTs with photo-cross-linked P(DPP2DT-TVT) channels as a function of 4Bx and 2Bx loading, noting poor retention for films prepared with 1 wt % of 2Bx. (h) Comparison of hole mobilities over time for pristine and crosslinked P(DPP2DT-TVT) PTFTs. (i) Hole mobilities of PTFTs with photopatterned P(DPP2DT-TVT) after soaking in various solvents. (j) Photograph of a 6 in. Si/SiO₂ wafer featuring P(DPP2DT-TVT) patterns. The polymer film was cast onto the wafer by bar-coating process before the photopatterning process. Reproduced with permission from ref 27. Copyright 2020 The Authors.

efficiently,¹² but still susceptible to reactions other than C–H insertion. Therefore, phenyl azides are further modified to have fluorine-substituted structures. This modification not only increases the lifetime of singlet nitrene but also increases the barrier of the ring expansion kinetics (k_{exp}) leading to desired intermolecular reactions (C–H insertion) only.^{16–19} When singlet nitrenes in a cross-linker containing more than two azide groups undergo C–H insertion reactions with adjacent alkyl chains, insoluble robust cross-linked state results.¹⁸ Herein, we call azide-based photo-cross-linkers “*n*-bridged crosslinker (*n*Bx)” when those are used to cross-link polymers or “*n*-ligand crosslinkers (*n*-LiXers)” when they are used to cross-link solution-processable light-emitting quantum dots (QDs), where *n* is the number of azide functional groups in the photo-cross-linker. For instance, 6Bx cross-linker has six azide groups at the terminals that can interconnect neighboring polymer chains or

QDs. Figure 1 illustrates the chemical design of *n*-bridged cross-linkers (Figure 1a), synthesized azide-based cross-linkers (Figure 1b), potentially cross-linkable electronic materials (Figure 1c), direct photopatterning process (Figure 1d), and applicable electronic devices (Figure 1e).

Several research groups have previously used a bifunctional phenyl azide of 2Bx as a photo-cross-linker for fabricating organic electronic devices.^{9,20,21} However, a large amount of 2Bx (>10 wt % relative to a target host material) is needed to obtain the desired photo-cross-linked networks in the host material layer due to its limited cross-linking efficiency ($\eta = 36\%$).^{10,17,22} This large amount of the photo-cross-linker might drastically affect the host materials' intrinsic electrical and optoelectronic properties. Thus, it is highly desirable to develop an even more efficient photo-cross-linker that requires only a minimal amount and thus can avoid detrimental effects on the original

optoelectronic properties of host materials and on the film morphology.²²

In our group, we have redesigned the existing bifunctional organic azide molecule (2Bx) to three-dimensional photo-cross-linking having multibridged azides such as 4Bx and 6Bx (Figure 1a,b). The incorporation of more cross-linkable azide units per molecule raises the cross-linking efficiency (η) which can be estimated by the following eq 1:

$$\eta = \sum_{j=2}^n \binom{n}{j} \cdot p^j \cdot (1-p)^{n-j} \cdot 100(\%) \quad (1)$$

where n is the total number of cross-linkable units, j is the number of units that participate in the cross-linking, and p is the cross-linking reaction yield of a cross-linkable unit. The cross-linking reaction yield (p) of an azide unit is approximately 60%.¹⁹ According to this equation, the cross-linking efficiencies for 2Bx, 4Bx and 6Bx are 36, 82, and 96%, respectively,¹⁸ which indicates that more efficient cross-linking occurs as the total number of cross-linkable units per molecule increases. In other words, we can successfully replicate the patterning process even with a much smaller amount of photo-cross-linkers when we use the multibridged azides. Moreover, we controlled the size of multibridged cross-linkers by introducing a bulky alkyl group (for instance, isopropyl group) into the fluorinated phenyl azide structure. The bulky groups let cross-linking reactions occur only with easily accessible side alkyl chains in the semiconducting polymers or the ligands of QDs, i.e., avoiding electronically active conjugated backbone in the semiconducting polymers or the core heavy atoms in QDs. This strategy has been successful in preserving the optical and electrical properties of their electronic materials even after cross-linking.²³ Besides, we also note that cross-linking efficiency depends on the following factors: cross-linker's miscibility with host materials, the kind of host materials, the wavelength and power of reaction-activating light source, and cross-linking atmosphere (inert atmosphere is desirable).

In this Account, we summarize our efforts toward the development of efficient azide-based cross-linking agents, which enable photopatterning of electronic materials such as semiconducting polymers and QDs without sacrificing the intrinsic optoelectronic properties of these materials. We also discuss the advantages and challenges of our approach along with future directions and the potential impact of azide-based cross-linking for photopatterning of electronic devices.

2. PHOTOPATTERNED THIN FILM TRANSISTORS

Solution-processing has great potential for the cost-effective manufacturing of multilayered electronic devices such as organic or polymer thin film transistors (OTFTs/PTFTs).^{24,25} Multiple techniques and setups are generally required to form several nicely patterned and seamlessly stacked electronic components in TFTs.⁶ As aforementioned, loss of optical or electrical properties arises commonly from the exposure of the solution-processed layers to chemicals in the subsequent processing steps.^{3,6,26} To resolve the issues, we synthesized a highly efficient cross-linker, 4Bx, having a tetrahedral shape with four photo-cross-linkable azide moieties, and utilized it to fabricate thin-film patterns of solution-processable polymer semiconductors, polymer gate dielectrics, and Ag nanoparticle-based conductors.²⁷ This approach enabled us to fabricate all-solution-processed, all-photopatterned PTFTs. Figure 2a displays a schematic representation alongside a photographic image of

fully photopatterned PTFTs fabricated on a plastic substrate. Figure 2b depicts the chemical structures of the materials utilized in this study, while Figure 2c illustrates the “direct photopatterning” process used for PTFT fabrication. In the direct photopatterning, each component layer of the devices, formed from a blend solution of electronic material hosts and 4Bx (1 wt % 4Bx for polymer hosts and 5 wt % 4Bx for Ag nanoparticles), was photo-cross-linked and the uncross-linked regions were rinsed away to give desired patterns with chemical and thermal stability. Successive layer formation resulted in the stacking of patterned functional material layers. An illustration of a three-dimensionally connected polymer film is shown in Figure 2d. Fourier transform infrared spectroscopy (FT-IR) confirmed the complete disappearance of azide stretching in the semiconducting polymer film after photo-cross-linking under 254 nm (Figure 2e). Film retention experiments demonstrated that using as little as 1 wt % of 4Bx to high-molecular-weight polymer hosts formed the intended thickness. Note that 1 wt % is the lowest loading for chemical cross-linking ever reported, proving that the 4Bx cross-linker having four cross-linkable moieties can indeed cross-link polymers efficiently (Figure 2f).^{10,28,29} Two-dimensional grazing incidence X-ray diffraction (GIXD) analysis on the *p*-type P(DPP2DT-TVTV) films photo-cross-linked by the use of 1 wt % 4Bx revealed well-ordered lamellar and strong π – π stacking structures with little change compared to those features of the pristine polymer films.⁴⁹ Importantly, the carrier mobility is well preserved at the use of 1 wt % 4Bx for the fabricated PTFTs (Figure 2g). Additionally, their shelf life and resistance to corrosive solvents are improved (Figure 2h,i). Lastly, wafer-sized photopatterning was readily achievable (Figure 2j). Conclusively, this study demonstrated the direct photopatterning method of using an efficient 4Bx cross-linker paves the way to all-solution-processed all-photo-patterned organic electronic devices without compromising their electrical properties.

In addition, for practical applications of PTFTs, important characteristics, including carrier mobility, operation voltage, and electrical/mechanical stability, should meet requirements. In particular, polymer gate dielectrics allowing high capacitance and low leakage current are essential for the development of wearable PTFTs. However, most polymer gate dielectrics have a low dielectric constant and a low density compared to inorganic dielectrics,^{25,30,31} leading to high operation voltage and electrical instability. Recent research has focused on polymer gate dielectrics functionalized with polar groups to increase the dielectric constant.³² However, this approach degrades device performance by disrupting the growth of organic semiconductor films and creating charge carrier trap sites.^{33,34} Polymer gate dielectrics like poly(methyl methacrylate) (PMMA) and polystyrene (PS) have been frequently used but they exhibited significant leakage currents due to their large free volumes and thermal motion of polymer chains when the thickness decreases below a certain threshold;³⁵ in turn, >0.5 μm thick polymer gate dielectrics are required. In this regard, it is crucial to develop a new approach for forming very thin polymer gate dielectrics that can still maintain low leakage current levels.

Cross-linking polymer chains through the formation of chemical bonds can significantly improve the insulating properties of polymer gate dielectrics by reducing leakage current and restricting thermal motion.^{27,36} Recently, we developed 6Bx having six photo-cross-linkable moieties and applied it to cross-link PMMA gate dielectrics in the fabricated PTFTs (Figure 3a,b). A nicely patterned ~50 nm thick PMMA

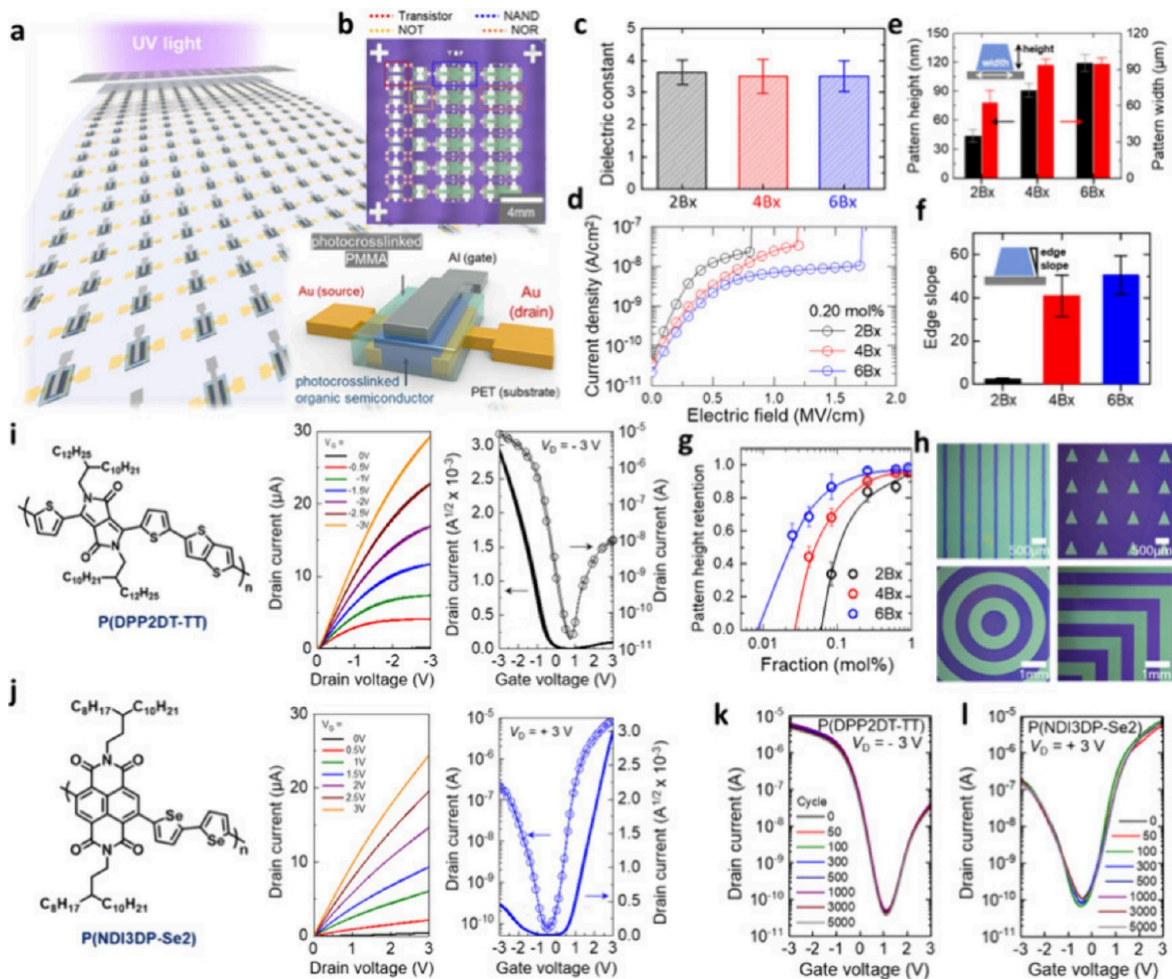


Figure 3. (a) Schematic representation of a PTFT array utilizing photo-cross-linked polymer gate dielectrics. (b) Optical microscopy images of PTFTs and various logic gates based on photo-cross-linked polymer gate dielectrics: (i) logic gates, (ii) unit transistor (red box), (iii) NAND (blue box), (iv) NOT (yellow box), and (v) NOR (orange box). (c) Dielectric constant of cross-linked PMMA dielectrics. (d) Current densities of PMMA films cross-linked with 2Bx, 4Bx, and 6Bx (0.20 mol %). (e) Pattern height, width, and (f) edge slope of PMMA patterns cross-linked with 2Bx, 4Bx, and 6Bx (0.06 mol %). (g) Retention of pattern height for cross-linked PMMA patterns with varying mole fractions of 2Bx, 4Bx, and 6Bx. (h) Optical microscopy images of PMMA patterns cross-linked with 6Bx (0.20 mol %). (i) Output and transfer characteristics of *p*-type P(DPP2DT-TT) PTFTs. (j) Output and transfer characteristics of *n*-type P(NDI3DP-Se2) PTFTs. (k) Transfer characteristics of *p*-type P(DPP2DT-TT) PTFTs after undergoing multiple bending cycles with 1% tensile strain. (l) Transfer characteristics of *n*-type P(NDI3DP-Se2) PTFTs after being subjected to multiple bending cycles with 1% tensile strain. Reproduced with permission from ref 18. Copyright 2022 American Chemical Society.

polymer gate dielectric layer was formed with minimal distortion, low leakage, and high electrical strength. A systematic study was conducted to find the photo-cross-linker structure-to-electrical property relationship on photo-cross-linked PMMA polymer gate dielectrics using three cross-linkers with different numbers of azide groups, i.e., 2Bx, 4Bx, and 6Bx (Figure 3c–f).¹⁸ The specific capacitance and dielectric constant are consistent regardless of the cross-linker type because the loaded amount is very low (Figure 3c). However, electric strength and leakage current are greatly improved with the number of cross-linkable units due to the cross-linking-induced dense PMMA states (Figure 3d). Moreover, the cross-linking efficiency of a cross-linker significantly affects the shape and retention of the patterned PMMA films, which correlates well with the number of azide groups and the cross-linker amount. The use of 0.20 mol % of 6Bx resulted in negligible film thickness changes after developing and allowed high-resolution patterning with high fidelity (Figure 3e–g). 6Bx enabled the formation of micro-patterns with a feature size of less than 10 μm and patterns of various shapes over a large area (Figure 3h).

PTFTs were fabricated using ~ 50 nm thick PMMA gate dielectric cross-linked with 0.20 mol % 6Bx. P(DPP2DT-TT) and P(NDI3DP-Se2) polymers were used for *p*-type and *n*-type PTFTs, respectively (Figure 3i,j). PTFTs having cross-linked very thin PMMA gate dielectric showed a significant increase in specific capacitance compared to a regular thick (~ 500 nm) PMMA layer, resulting in a lower operating voltage (~ 3 V). Also, *p*- and *n*-type PTFTs exhibited excellent hole and electron mobilities of 12.42 and 10.11 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, with excellent mechanical stability (Figure 3k,l). Furthermore, logic circuits (NOT, NAND, NOR gates) and ring oscillators were successfully demonstrated using these basic PTFTs.¹⁸ In addition, GIXD measurements were conducted to explain the remarkably improved carrier mobilities in the PTFT devices with cross-linked thin PMMA gate dielectrics.¹⁸ The analysis showed that P(DPP2DT-TT) films had edge-on-oriented polymer chains for efficient in-plane charge transport. P(NDI3DP-Se2) films exhibited well-aligned face-on-oriented polymer chains, which contributed to the formation of well-developed charge transport channels. Thermal annealing after

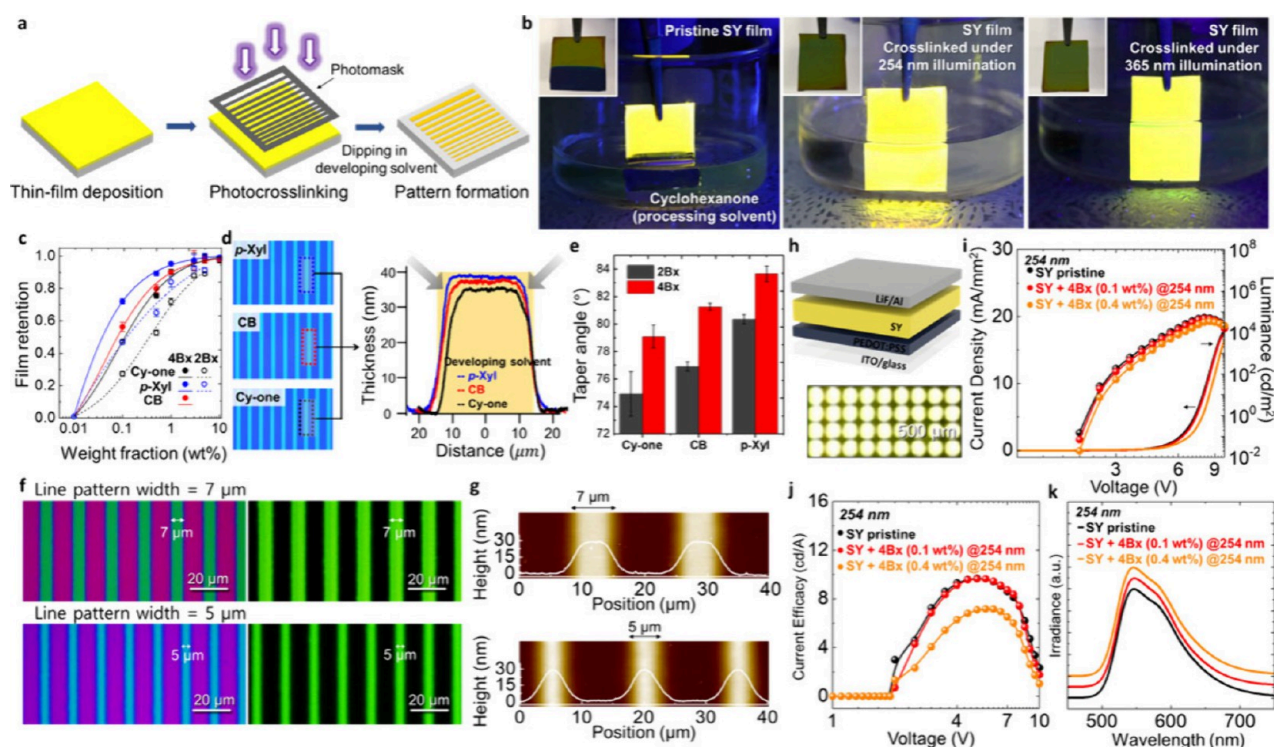


Figure 4. (a) Diagram illustrating the photopatterning process of polymer semiconductors. (b) Images of SY films partially immersed in cyclohexanone, with insets showing photographs of the dried SY films after partial immersion. (c) Retention characteristics of SY films cross-linked with varying amounts of 4Bx and 2Bx, developed using different solvents. (d) Optical microscopy images of photopatterned SY films using 4Bx, developed with various solvents. (e) Summary of the tapered angles of the photopatterned SY films. (f) Optical (left) and fluorescence (right) microscopy images of SY line patterns. (g) Height profiles of the patterns shown in (f), measured using atomic force microscopy. (h) Schematic of a polymer-based OLED structure and an electroluminescent (EL) image of photopatterned SY films during device operation. The scale bar represents 500 μm . In this device, only the SY emissive layer (EML) was patterned, while the electrodes and hole injection layer (HIL) remained unpatterned. (i) Current density vs. voltage plot, (j) current efficiency vs. voltage plot, and (k) normalized EL spectra (with offset) for OLEDs with SY EMLs photo-cross-linked under different conditions. Reproduced with permission from ref 44. Copyright 2021 American Chemical Society.

cross-linking the very thin PMMA layer further enhanced the dominant molecular alignments of both semiconducting polymers, with increased edge-on alignment for P(DPP2DT-TT) and face-on alignment for P(NDI3DP-Se2). In other words, the interconnection of semiconducting polymer chains and PMMA chains through 6Bx cross-linker at the interface promotes anisotropic alignment, resulting in the growth of more ordered charge transport pathways. Additionally, temperature (T)-dependent transistor measurements revealed reduced energy barriers and trap density for charge transport and enhanced electronic coupling due to the structural changes induced by cross-linking and thermal annealing.¹⁸ Overall, it is demonstrated that the use of a highly efficient cross-linker in the fabrication of PTFTs can contribute to the realization of wearable electronic devices based on high mobility, high stability, and low-voltage operating PTFTs.

3. PHOTOPATTERNED ORGANIC LIGHT-EMITTING DIODES

Commercial OLEDs currently rely on fabrication based on vacuum deposition using a shadow mask. However, this method has limitations in achieving high-resolution ($<10\ \mu\text{m}$) patterns and high uniformity over large areas and requires high cost in display production. Accordingly, alternative processing methods are being sought to overcome these challenges via solution-processing.^{37–39} In fact, each pixel of an OLED display consists of multiple stacked functional layers, such as electrodes, carrier

injection layers, carrier transport layers, and emissive layers. Currently, it is still challenging to create well-defined pixels of different solution-processable materials, particularly for RGB luminophores, because the dissolution or chemical degradation of the predeposited underlying layer occurs during subsequent solution-processes. In this regard, photopatterning of solution-processable organic layers using a light-triggered cross-linking reaction can be a potential solution for the generation of high-resolution pixelated OLEDs. This approach can stack multiple layers through iterative solution-processes,⁴⁰ and can generate high-resolution patterns with feature sizes smaller than a few micrometers.

Two photo-cross-linking approaches have been previously developed for cross-linking reactions between organic molecules or polymers of interest: (i) incorporating photo-cross-linkable units in the alkyl side chains⁴¹ and (ii) blending photo-cross-linkable reagents inside the host organic materials.⁴¹ The former approach requires multistep synthesis of cross-linkable materials for each layer.^{11,42} Moreover, the incorporated cross-linkable units can have detrimental effects on the optical/electrical properties of the target layer materials.⁴⁰ The latter approach, using phenyl azides as photo-cross-linkable reagents, has shown advantages such as avoiding the generation of residual chemical species or morphological changes in the film.⁴³ However, this approach has often required a high loading of a cross-linker (e.g., $>7\ \text{wt}\%$ 2Bx) to achieve a fully cross-linked polymer film²⁷ and has not been used in the high-resolution ($<10\ \mu\text{m}$) photopatterning of light-emitting polymer semiconductors.

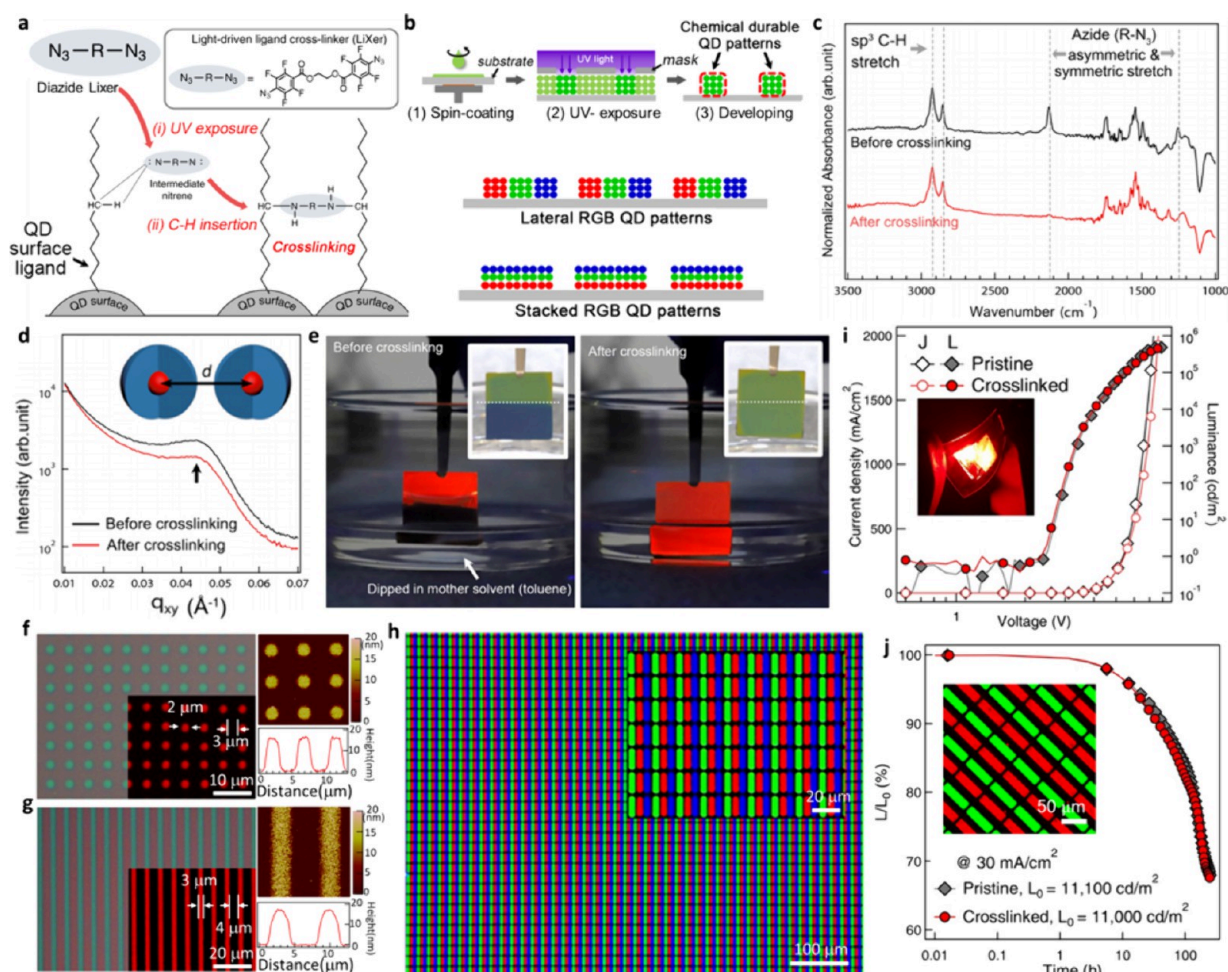


Figure 5. (a) Diagram illustrating the ligand cross-linking process between adjacent QDs, based on the C–H insertion reaction of the nitrene group in LiXer, with the inset showing the chemical structure of LiXer. (b) Illustration of the photopatterning process for QDs using LiXer. (c) FT-IR spectra normalized to the sp^3 C–H stretch peak at 2924 cm^{-1} and offset for clarity. (d) GI-SAXS patterns comparing 13 nm CdSe/CdZnS QD films with 5 wt % LiXer before (black) and after (red) UV exposure (254 nm , 0.4 mW cm^{-2}). (e) Photographs of a cross-linked QD film containing 5 wt % LiXer (right) and a pristine QD film (left), partially immersed in toluene, the casting solvent. (f, g) Optical, fluorescence (inset), and AFM images, along with height profiles, of dot ($2\text{ }\mu\text{m}$ diameter, $3\text{ }\mu\text{m}$ spacing) and line ($3\text{ }\mu\text{m}$ width, $4\text{ }\mu\text{m}$ spacing) patterns made from 13 nm red-emitting CdSe/CdZnS QDs. (h) Fluorescence images of RGB QD patterns created via consecutive photopatterning processes using RGB QDs, with subpixel dimensions of $4\text{ }\mu\text{m} \times 16\text{ }\mu\text{m}$, corresponding to a resolution exceeding 1400 ppi. The inset shows a magnified section of Figure 6h. (i) Plots of current density (J), voltage (V), and luminance (L). (j) Temporal changes in relative luminance of QD-LEDs with pristine (gray diamonds) and cross-linked (red circles) films, where L_0 represents the initial luminance. Reproduced with permission from ref 56. Copyright 2020 The Authors.

We explored the use of our cross-linker, 4Bx,²⁷ for the photopatterning of Super Yellow (SY) polymer films.⁴⁴ SY is an extensively used light-emitting polymer semiconductor for polymer-based OLEDs. Photopatterning of the SY film was conducted by spin-coating, photo-cross-linking, and developing processes (Figure 4a). The SY film was effectively cross-linked with minimal loading of the highly efficient cross-linker, 4Bx (0.1 and 0.2 wt % of 4Bx when using 254 and 365 nm light sources, respectively) (Figure 4b,c). The solubility contrast between the cross-linked and uncross-linked regions of the polymer was maximized by selecting developing solvents with higher solubility differences (Figure 4c,d). Furthermore, 4Bx demonstrated an even higher cross-linking efficiency when compared with its lower analog 2Bx, as evidenced by good film retentions for the 4Bx use (Figure 4e). The use of 4Bx also exhibited a taper angle higher than that of the use of 2Bx and *o*-xylene was found to be optimal as a developing solvent because of its finite solubility. Finally, photopatterned SY films up to a $5\text{ }\mu\text{m}$ scale were generated, which was confirmed by optical, fluorescence,

and atomic force microscopies (Figure 4f,g). Electroluminescence (EL) properties of cross-linked SY films were evaluated by analyzing the performance of OLEDs based on these films. The EL devices exhibited current density–voltage–luminance characteristics and EL spectra, which are nearly the same as those properties from the pristine (i.e., un-cross-linked) SY-based EL devices. These results indicate that cross-linking with 0.1 wt % 4Bx under 254 nm illumination had a minimal effect on the EL characteristics (Figure 4h–k). However, an increase in 4Bx content (0.4 wt %) resulted in a positive voltage shift and a lower maximum current efficacy (Figure 4i,j). The work highlights that the choice of an optimal cross-linking condition, especially the amount of cross-linkers, is critical in patterning light-emitting polymer films while preserving their EL properties in OLED applications, and our approach can be potentially crucial in creating high-resolution OLED displays in the future.

In addition, we developed a cost-effective solution process using 6Bx-stabilized orange and cyan luminophore strip patterns to reduce efficiency loss and color variations for white organic

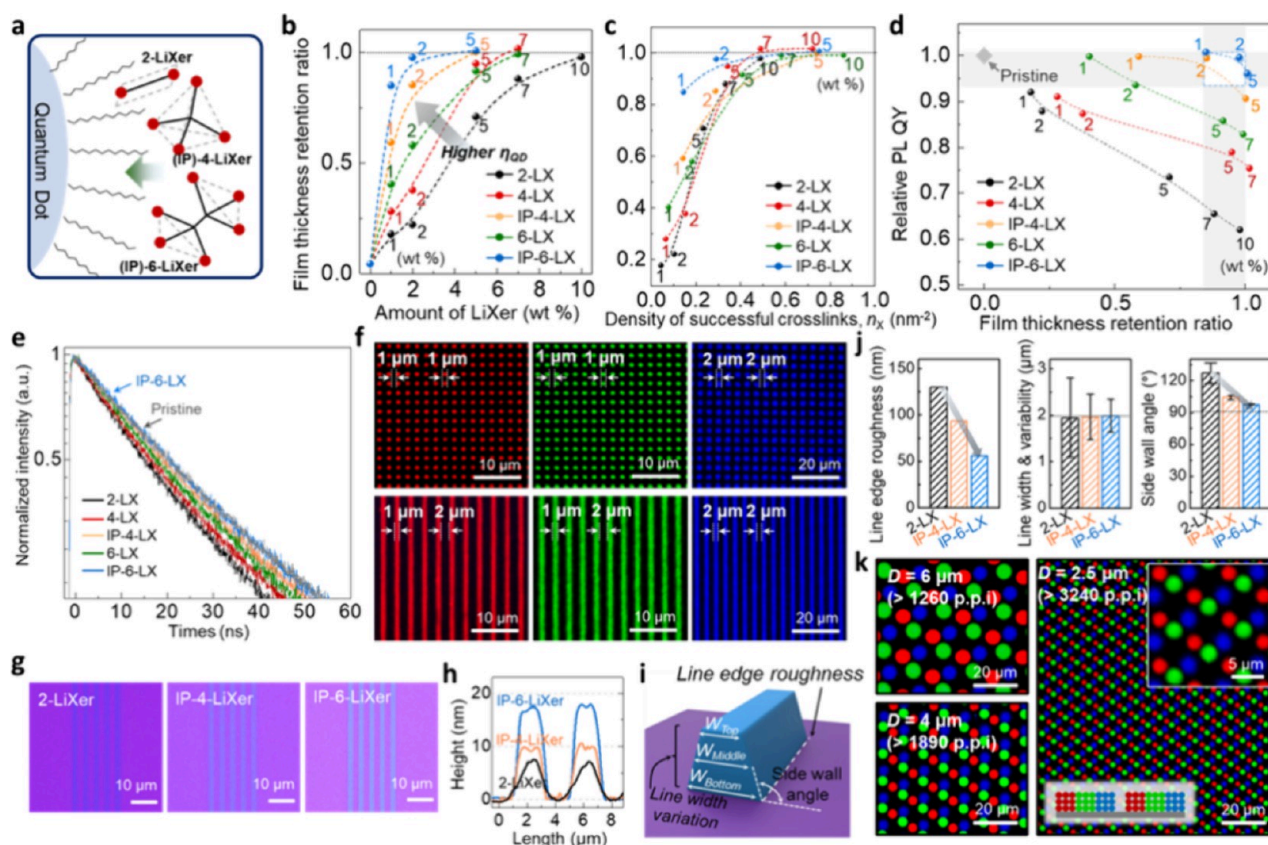


Figure 6. (a) Illustration depicting the limited accessibility of sterically bulky branched n -LiXers to the QD surface. (b) Film thickness retention ratio (FRR) of InP/ZnSeS QD films cross-linked with various branched LiXers. (c) Relationship between FRR and the number density of effective crosslinks (n_x) within the QD film. (d) Relative PLQY as a function of FRR for QD films cross-linked with different branched LiXers, normalized to the PLQY of pristine QD films (absolute PLQY = 65%). The blue-dotted square highlights nondestructive photo-cross-linking conditions for InP/ZnSeS QD films, with numbers indicating LiXer contents (wt %). (e) PL decay curves of pristine (gray) and photo-cross-linked InP/ZnSeS QD films, with the inset showing PLQYs derived from $1/e$ decay lifetimes. (f) Fluorescence microscopy images of dot (top; $1\ \mu\text{m}$ diameter, $1\ \mu\text{m}$ spacing) and line patterns (bottom; $1\ \mu\text{m}$ width, $2\ \mu\text{m}$ spacing) of red-, green-, and blue-emitting QD films created using 1 wt % IP-6-LiXer. (g) Optical microscopy images and (h) height profiles of green-emitting InP/ZnSeS QD line patterns cross-linked with 1 wt % of 2-LiXer, IP-4-LiXer, and IP-6-LiXer, with line patterns of $2\ \mu\text{m}$ width and spacing. (i) Diagram of a line pattern showing key physical parameters. (j) Comparison of average line edge roughness, line width variability, and sidewall angle for QD line patterns prepared using 1 wt % of 2-LiXer, IP-4-LiXer, and IP-6-LiXer. (k) Fluorescence microscopy images of RGB QD patterns generated through iterative photopatterning. Subpixel diameters of $6\ \mu\text{m}$, $4\ \mu\text{m}$, and $2.5\ \mu\text{m}$ correspond to resolutions of approximately 1260, 1890, and 3240 ppi, respectively. ZnSe/ZnS QDs (core radius of 3.0 nm and shell thickness of 1.8 nm), InP/ZnSeS QDs (core radius of 1.2 nm and shell thickness of 2.8 nm), and InP/ZnSeS QDs (core radius of 1.9 nm and shell thickness of 1.6 nm) were used for blue, green, and red patterns, respectively. Reproduced with permission from ref 23. Copyright 2022 Wiley-VCH GmbH.

light-emitting diodes (WOLEDs).^{44–50} Importantly, this approach enabled precise tuning of the color temperature. A more detailed description of this work is presented in the [Supporting Information](#).

4. PHOTOPATTERNED QUANTUM-DOT LIGHT-EMITTING DIODES

QDs exhibit exceptional properties such as ultrahigh color purity and near-unity luminescence quantum yield, making them a promising photon source for future displays.⁵¹ After the successful utilization of photoluminescence from QDs in current commercial devices, the focus is now shifting toward launching QD-based displays using their electroluminescence (EL).^{52,53} However, to realize EL displays, precise processing methods for accurately positioning red, green, and blue QDs within pixels across large areas need to be developed. Conventional methods of patterning using photoresists have limited applicability owing to the destructive processing, resulting in the degradation of optical and electrical properties; therefore, alternative ap-

proaches like inkjet printing and microcontact printing have been pursued, but their achievable resolutions are yet to be improved.⁵⁴ As an alternative, utilizing cross-linking agents to cross-link QDs in a well-defined area can be considered a promising strategy. Exposing a blend film of QDs and azide cross-linking agents to UV light demonstrated the formation of chemically robust QD networks.⁵⁵ The major advantage of this approach, so-called direct photopatterning, is that high-resolution patterns of luminescent QDs are attainable while preserving their optical properties with a sophisticated control of the employed cross-linker amount.

First, we demonstrated QD patterns with subpixel sizes and resolutions exceeding 1400 pixels per inch (ppi) using a small amount (less than 5 wt %) of a bifunctional light-driven ligand cross-linker, ethane-1,2-diyl bis(4-azido-2,3,5,6-tetrafluorobenzoate) (2-LiXer).⁵⁶ Figures 5a and 5b demonstrate a direct photopatterning method and cross-linking mechanism for QDs using 2-LiXer. 2-LiXer enables the direct utilization of high-quality QDs with long alkyl chains, allowing for the formation of chemically robust QD films without degrading their lumines-

cence properties. FT-IR and grazing-incidence small-angle X-ray scattering (GISAXS) analysis confirmed the successful cross-linking of QDs without significant alteration of interparticle distance (Figure 5c,d). Cross-linking the ligands in QD films provides structural robustness, as demonstrated by the resistance of cross-linked films to dissolution in toluene compared to pristine films (Figure 5e). This robustness enabled the creation of multicolored QD patterns through repeated photo-cross-linking reactions and rinsing steps, with a low 2-LiXer concentration of 2 wt % being sufficient to ensure film stability. Dot patterns with a diameter of 2 μm and a spacing of 3 μm , as well as line patterns with a width of 3 μm and a spacing of 4 μm , were successfully achieved (Figure 5f,g). Further, red/green/blue (RGB) QD patterns (fluorescence images are shown in Figure 5h), with each individual pattern measuring 4 μm by 16 μm , were also achieved. When three RGB patterns, spaced 2 μm apart, are combined, they form a unified 18 $\mu\text{m} \times 18 \mu\text{m}$ RGB square pixel. This configuration achieves a display pixel resolution of over 1400 ppi and exceeds the pixel resolutions of current commercial OLED displays. Moreover, QD-LEDs were fabricated using photo-cross-linked QD films in an inverted structure. The emission layer (EML) consisted of a 30 nm-thick cross-linked QD film prepared from red-emitting CdSe/CdZnSe/ZnSeS QDs dispersed in the presence of 1 wt % 2-LiXer. The electrical and optoelectronic characteristics of the QD-LEDs incorporating the cross-linked QD layer showed no significant difference compared to those with pristine QD layers (Figure 5i,j). This work demonstrated that the emission and electrical properties of the QD films can be well-preserved even after the photo-cross-linking and photopatterning process.

Next, we further modified the chemical structures of azide-based cross-linkers *n*-LiXers containing bulky aliphatic groups to investigate the effects of the number of azide groups and the size of cross-linkers on the photopatterning of heavy metal-free QDs.²³ The approach of the *n*-LiXers to the surface ligands of InP/ZnSeS QDs are presented in Figure 6a, illustrating the larger dimensional cross-linkers have limitation of directly contacting the core of QDs, i.e., better preservation of the intrinsic properties of the QD core. The ligand cross-linked QD films were created by photopatterning of the InP/ZnSeS QD films by selectively exposing them to UV light through a photomask and developing UV-unexposed regions. A systematic study correlating the structure of *n*-LiXers to the structural and photophysical characteristics of the InP/ZnSeS QD patterns was conducted. It was interesting to find that 2-LiXers resulted in a significant decrease in the luminescence efficiency of InP/ZnSeS QDs, unlike the case of photo-cross-linking CdSe/CdZnSe/ZnSeS QDs.¹⁷ It is likely that 2-LiXers are linear and small-sized so that some of them can be caught between surface ligands and have direct contact with the QD core surface; then, upon UV exposure photogenerated nitrenes can react with the QD core surface and form defects, which is a source of luminescence quenching.⁵⁷ By contrast, we found that the degradation of the optical and electrical characteristics of QDs and QD films can be avoided by incorporating multiple azide-containing cross-linkers and can be further prevented by employing bulky isopropyl groups in the phenyl azide moieties. The increasing *n*, as well as the number of introduced IP groups in the LiXers resulted in higher film thickness retention ratios (FRRs) (Figure 6b), since the QD cross-linking efficiency (η_{QD} , the probability of a single cross-linker successfully linking neighboring QDs) increases with an increase in the number of cross-linkable units (Figure 1d). FRR depends on the number density of successful cross-

links within the QD film (n_{x}), and a value of $n_{\text{x}} > 0.5 \text{ nm}^{-2}$ is required for fully cross-linked QD films with high FRR values (Figure 6c). However, increasing the weight percent of LiXers degrades the photoluminescence quantum yields (PLQYs) of the QD films, indicating a trade-off between the FRR and PLQY (Figure 6d). Nevertheless, it should be noted that the IP-*n*-LiXers having multiple azides and IP groups showed higher FRRs and higher PLQYs than did the corresponding *n*-LiXers. Importantly, the IP-6-LiXer at an optimized concentration of 2 wt % achieved both high FRR and relative PLQY values close to unity for cross-linked QD films, demonstrating the non-destructive direct photopatterning of luminescent heavy metal-free QDs (Figure 6d,e). Optical microscopy images and height profiles of the photopatterned QD films exhibited enhanced structural clarity and fidelity with higher *n*-LiXers (Figure 6f–j). Statistical assessments confirmed the excellent performance of IP-*n*-LiXers in terms of line edge roughness, line width variability, and sidewall angle of QD patterns compared to 2-LiXer (Figure 6h–j). The enhanced pattern clarity enabled the fabrication of well-defined line and circular patterns with different QD colors, achieving high pixel resolutions suitable for generating hyperrealistic images (Figure 6k). It should be noted that our direct photopatterning approach using IP-6-LiXer is applicable to various QDs, provided they are passivated with ligands containing C–H based alkyl chains. In addition, QD-LEDs with a photo-cross-linked InP/ZnSeS QD EML using IP-6-LiXer exhibited nearly identical device performance to those with pristine QD layers in terms of EL spectra, current–voltage characteristics, luminance, and EQE.²³ The operational stability of the QD-LEDs with the photo-cross-linked QD EML was even better than those based on the pristine QD layers.²³ The IP-6-LiXer cross-linker preserved the optical and electrical characteristics of the QD films, making it a promising material for optoelectronic devices utilizing QDs. We conclude that sophisticated control over the number of cross-linking groups and molecular geometry is critical for the nondestructive fabrication of heavy metal-free QD pixels.

5. CONCLUSIONS AND OUTLOOK

We comprehensively summarize our efforts in applying azide-based cross-linkers to the fabrication of high-resolution photopatterned devices, including TFTs, OLEDs, and QD-LEDs. Azide cross-linkers-based processing affords versatile and precise patterning for electronic materials with high resolution, high compatibility with diverse materials, and scalability for large-scale manufacturing. In particular, carefully designed multibridged photo-cross-linkers have demonstrated impressive parallel and vertical stacking of electronic layers without compromising optical and electrical properties, thanks to their excellent cross-linkability even when used in small amounts.

Despite this success, many other issues remain to be solved. We are undertaking to elaborate the structural design of azide-based cross-linkers for electronic interlayers, such as hole-injection layer, hole-transport layer, electron-transport layer, electrodes, and for band bending-assisted exciton scissoring materials.^{58,59} Fabrication of these layers through the patterning process will be beneficial, especially for full-color and high-resolution electroluminescent devices (such as OLEDs and QD-LEDs), which resolve crosstalk issues between different color pixels. We are also synthesizing stretchable cross-linkers that enable the fabrication of flexible and stretchable patterned electronic devices. We are also exploring the use of our multiarmed cross-linkers in organic thermoelectric devices to

maximize thermoelectric performance and enhance stability and interface control.⁶⁰ Moreover, we are developing low-temperature-activatable cross-linkers with innovative chemical structure designs to resolve concerns related to azide activation since the azide-activating UV light may cause light-induced damage to some UV-sensitive organic and inorganic materials. Azides can also be activated by thermal stimulation, but the required temperatures are higher (>180 °C), which may result in chemical and physical degradation of host materials. Furthermore, we are working to integrate azide cross-linker-based processing with other advanced printing techniques, such as inkjet printing and 3D printing, which will open new avenues for fabricating complex electronic structures and devices. Overall, we believe that new functional cross-linker-based patterning of various electronic materials will have significant implications in realizing fully solution-processed future electronics.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/accountsmr.4c00365>.

Additional detailed discussion of our work on color-temperature tuning of white organic light-emitting diodes (WOLEDs) (PDF)

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Notes

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