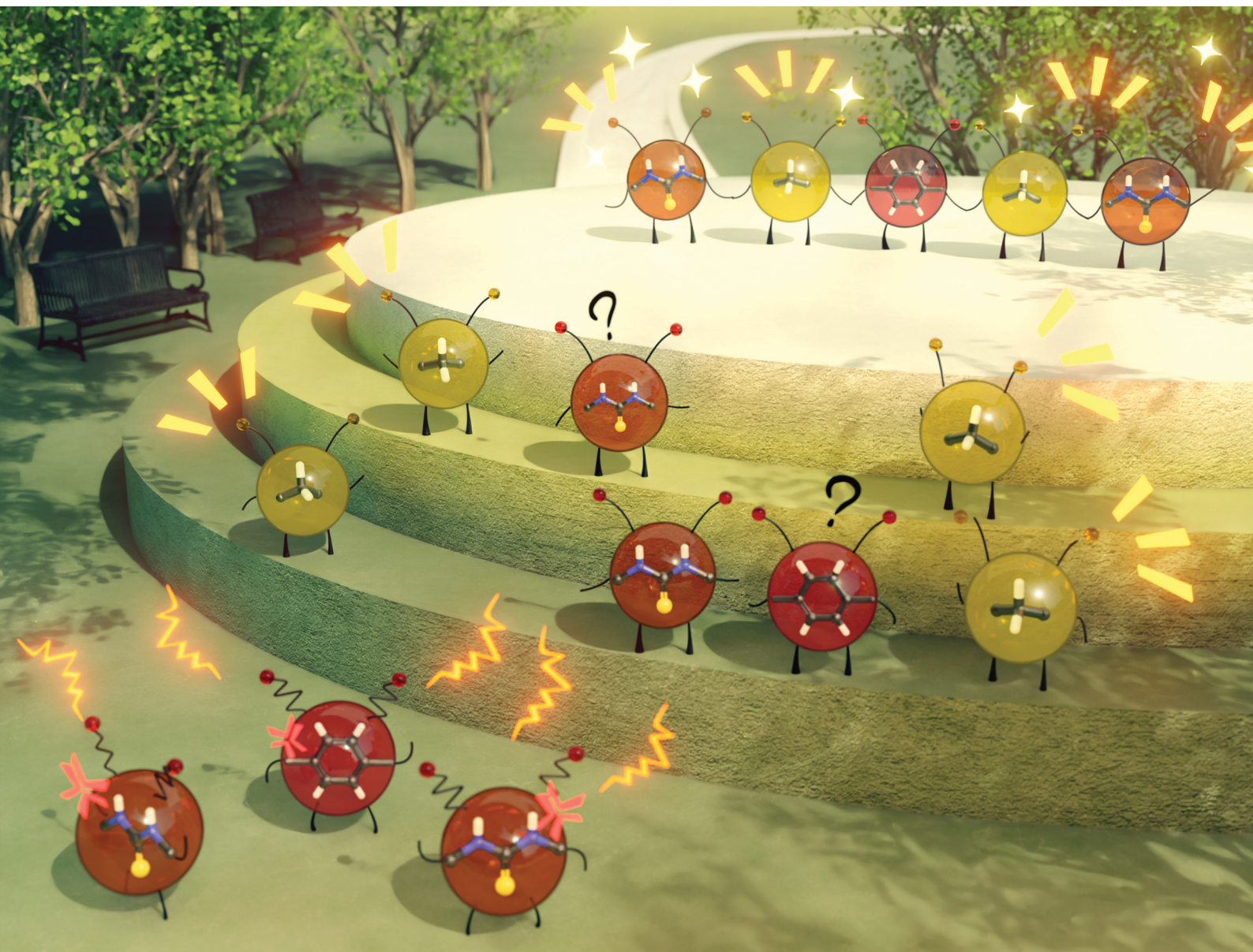


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Bleaching effect of high refractive index xylylic poly(thiourea)s with “de-conjugated” polarizable hydrogen bonds

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Poly(*p*-xylylene thiourea) (pX-PTU) exhibits high visible-light transparency (%*T* ≳ 99), a high refractive index ($n_D = 1.71$), and a reasonable Abbe number ($\nu_D = 26$) owing to “de-conjugated” hydrogen bonds, which inhibit orbital interactions between the polarizable phenylene and thiourea units through sandwiched methylene spacers. Upon blending pX-PTU with all-aromatic poly(thiourea)s, their refractive index increased up to $n_D = 1.80$.

High refractive index polymers (HRIPs) typically exhibit refractive indices (RI) above 1.7 and are essential in various optoelectronic applications, including lighting devices, waveguides, and augmented/mixed reality (AR/MR).^{1–5} To date, numerous HRIPs have been developed based on the Lorentz–Lorenz equation, which requires optimizing high polarizability and small molecular volume to achieve the desired RI and transparency at the target wavelength.^{2,4} The most common HRIP categories are sulfur-containing polymers, such as poly(phenylene sulfide)s,^{4,6–10} sulfur-rich polymers,^{3,11–13} and thioacetal-containing polymers.^{14,15} In particular, HRIPs with excessive sulfur content or conjugated π -skeletons achieve ultrahigh RI (over 1.8),^{11,16,17} but they are colored due to the orbital interactions among π -skeletons and/or sulfur lone pairs (*e.g.*, n - π interactions¹⁸). To address this empirical dilemma, we previously developed hydrogen-bonding (H-bonding) poly(phenylene sulfide)s to achieve both ultrahigh RI ($n_D \sim 1.80$ – 1.85) and visible-light transparency.^{19,20} The key factor lies in the reduced free volume, which enhances the RI without compromising UV-visible (UV-vis) transparency. We further extended this concept to all-aromatic poly(thiourea)s (PTUs) featuring multiple and polarizable H-bonds, exhibiting better RI ($n_D \sim 1.7$ – 1.8) and flexibility owing to strengthened PTU networks.^{21,22} Also, other researchers have recently reported diverse high-RI PTU structures.^{23,24} However, although all-aromatic PTU thin films are

nearly colorless, their transparency remains low (%*T* ≥ 92, 1 μm thick) owing to the direct coupling of polarizable thiourea and aromatic rings, which leads to excessive orbital interactions resulting in near-UV absorption and small Abbe numbers ($\nu_D = 11$ – 18).²¹

In this study, we provide a new concept, termed as “de-conjugated” polarizable H-bonds, to significantly enhance the transparency of high-RI PTUs (Fig. 1). The key design is poly(xylylene thiourea) (X-PTU), which contains a sandwiched methylene spacer that separates polarizable aromatic and thiourea groups, thereby inhibiting orbital interactions. In particular, *p*-substituted X-PTU (**pX-PTU**) exhibited amorphous and thermal properties comparable to those of the all-aromatic PTUs, while displaying improved transparency (%*T* ≥ 99) and a higher Abbe number ($\nu_D = 26$) with its high RI ($n_D = 1.71$) maintained (Fig. 1, right). In addition, **pX-PTU** showed good miscibility with all-aromatic poly(1,3-phenylene-*alt*-1,4-phenylene thiourea) (**mpPh-PTU**), producing simply blended transparent films with an enhanced T_g and well-balanced optical properties ($T_g = 164$ °C, $n_D = 1.80$, $\nu_D = 17$). Overall, this study highlights the potential of the “de-conjugated” H-bonding X-PTU and its polymer blends as a rational approach to simultaneously maximize various properties (*e.g.*, RI, Abbe numbers, and transparency) for versatile optoelectronic polymers.

The X-PTUs were synthesized following our previous report,²¹ involving the polycondensation of xylylene diamines (XDA) and 1,1-thiocarbonyl diimidazole (Schemes S1 and S2).

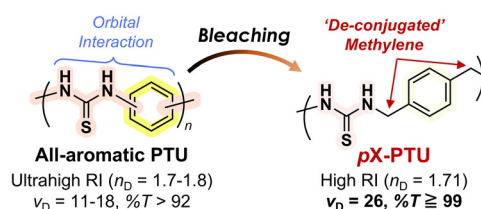


Fig. 1 The concept of “de-conjugated” polarizable H-bonds: from all-aromatic PTU²¹ (left: prior work) to **pX-PTU** (right: this work) to bleach high-RI PTUs.

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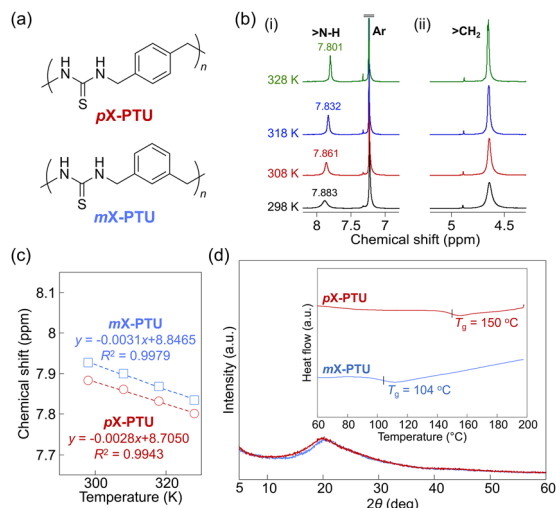


Fig. 2 Properties of X-PTUs. (a) Chemical structures of *p*X-PTU and *m*X-PTU. (b) ¹H VT-NMR of *p*X-PTU (i) at 8.2–6.8 ppm (>N–H and aromatic signals) and (ii) at 5.2–4.3 ppm (methylene signals). (c) Temperature dependence of >N–H chemical shifts in ¹H VT-NMR. (d) XRD profiles (inset: DSC thermograms at a scan rate of $20^\circ\text{C min}^{-1}$).

Two *m*- and *p*-substituted PTU isomers (*m*X-PTU and *p*X-PTU) were obtained as high-molecular-weight polymers ($M_w \sim 10^5$), owing to the higher nucleophilicity of XDAs compared with that of all-aromatic diamines (Fig. 2a). The resulting X-PTUs were characterized by ¹H and ¹³C NMR spectroscopy, showing signals of thiourea, aromatic, and methylene groups (Fig. S1–S4). The IR spectra indicate two N–H conformations of thiourea ($\nu_{\text{N–H}}(\text{trans/trans})$: $\sim 3270\text{ cm}^{-1}$ and $2\delta_{\text{N–H}}(\text{cis/trans})$: $\sim 3055\text{ cm}^{-1}$), suggesting the presence of randomized H-bond networks (Fig. S5). Upon increasing the temperature, the ¹H variable-temperature (VT) NMR spectra of the X-PTUs showed an upfield shift exclusively for the H-bonding amino signals (7.93–7.80 ppm) (Fig. 2b and Fig. S6). Notably, *p*X-PTU exhibited lower temperature dependence ($-2.8 \times 10^{-3}\text{ ppm K}^{-1}$) than *m*X-PTU ($-3.1 \times 10^{-3}\text{ ppm K}^{-1}$) and previously reported phenylene-PTUs ($< -3.5 \times 10^{-3}\text{ ppm K}^{-1}$)²¹ (Fig. 2c). These results indicate that *p*X-PTU contains stronger and more high-temperature-resistant intermolecular H-bond network.

Regarding the crystalline properties, the X-ray diffraction (XRD) profiles indicate an amorphous nature of X-PTUs, which can be attributed to the zig-zag H-bonds of the thiourea arrays (Fig. 2d). *X*-PTU exhibited good thermostability, with both an adequate T_g ($> 100^\circ\text{C}$) and a high pyrolysis temperature ($T_{d5} \sim 240\text{--}250^\circ\text{C}$), significantly surpassing those of phenylene-PTUs ($T_g \sim 150^\circ\text{C}$, $T_{d5} \sim 180^\circ\text{C}$)²¹ (Fig. 2d inset, Fig. S7). This superior thermostability can be attributed to the deconjugated X-PTU structure containing methylene spacers, which enhance the bond stability (dissociation energy) of the C–N bonds, similar to the effect observed in aromatic/xylylic poly(dithiourethane)s.²⁵ Among the X-PTUs, *p*X-PTU showed a significantly higher T_g (150°C) than *m*X-PTU ($T_g = 104^\circ\text{C}$), owing to the stronger and more temperature-resistant interchain H-bonds in the linear-shaped *p*-phenylene skeleton compared with the bent-shaped *m*-phenylene unit.

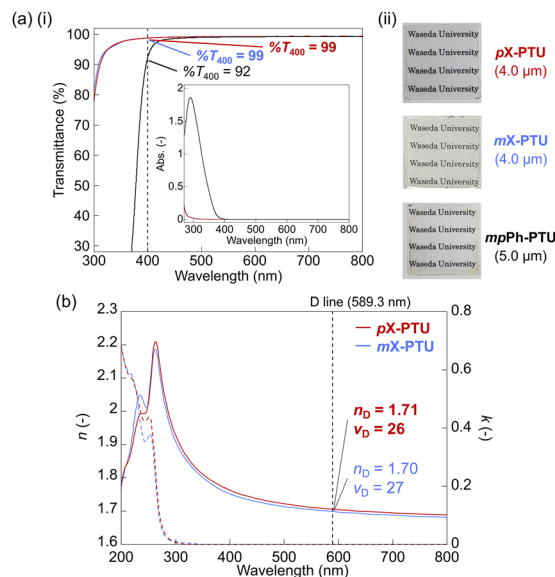


Fig. 3 Optical properties of X-PTUs. (a) (i) Normalized UV-vis spectra for the films (thickness: $1\ \mu\text{m}$) of X-PTUs and *mpPh*-PTU (inset: UV-vis absorbance spectra of 0.1 mM solution in DMF). (ii) Photographs of PTU thin films on glass substrates and their thickness. (b) RI spectra: n (solid line) and k (dotted line).

Their optical properties were investigated to confirm the introduction effect of “de-conjugated” H-bonds (Fig. 3). The solution UV-vis spectra displayed that the X-PTUs exhibit superior visible-light transparency compared with *mpPh*-PTU, accompanied by a blue shift in near-UV absorption (Fig. 3a inset). This behavior can be attributed to the absence of orbital interactions between the lone pairs/ π -electrons of the thioureas and phenylene rings upon the introduction of methylene spacers. To gain molecular-level insight, density functional theory (DFT) calculations were conducted on the model compounds of each polymer (Fig. S8). The orbital geometries of the phenylene-PTU models exhibited a widely distributed highest occupied molecular orbital (HOMO), which strongly overlapped with the lowest unoccupied molecular orbital (LUMO). In contrast, the X-PTU model showed a narrower distribution of continuous HOMO orbitals and less HOMO–LUMO geometry overlap. The estimated UV-vis spectra by time-dependent (TD) DFT calculations reproduced a pronounced blue shift in the near-UV absorption for the X-PTU models (Fig. S9). Therefore, the effect of “de-conjugated” methylene spacers in X-PTUs can be rationalized as the suppression of orbital interactions between thioureas and phenylene rings.

X-PTU thin films were also prepared *via* drop-casting or spin-coating, exhibiting colorless and visually transparent features (Fig. 3a), and the *p*X-PTU film displayed a fluorescence emission under UV irradiation (Fig. S10), as observed in typical PTUs.²⁶ Their UV-vis spectra display higher near-UV-vis transparency ($\%T \geq 99$) than those of aromatic PTUs, owing to the bleaching effect in the X-PTUs (Fig. 3a(i) and Fig. S11). Following the introduction of methylene spacers, the X-PTUs exhibited lower RI ($n_D = 1.71$ (*p*X-PTU) and 1.70 (*m*X-PTU)) than previously reported phenylene-PTUs ($n_D \sim 1.8$)²¹ because of the



decrease in the unit polarizability (Fig. 3b). However, their RI remained within the range of typical HRIPs,^{2,4} while the Abbe numbers were markedly improved ($\nu_D = 26$ (**pX-PTU**) and 27 (**mX-PTU**)) compared with those of the reported phenylene-PTUs ($\nu_D \sim 11$ –15)²¹ and dimethyl-substituted PPS with a similar RI ($n_D = 1.69$, $\nu_D = 18$).²⁷ These trends follow the classical Kramers–Kronig relationship,²⁸ which explains that suppressing the near-UV absorption in X-PTUs results in a higher ν_D . Furthermore, despite the low UV stability of aromatic PTUs ascribed to the presence of reactive C=S bonds²⁹ that induced lower transparency and RI (Fig. S12 and S13), the optical properties of **pX-PTU** were less deteriorated after the UV treatment than those for **mpPh-PTU**, thanks to the “de-conjugated” xylylene unit with less orbital interactions. In addition, there has been minimal change in RI and transparency of **pX-PTU** after the high-temperature or humid exposure (difference of % $T_{400} \sim 1\%$, $n_D \sim \pm 0.01$) (Fig. S14–S17), attributed to the high hydrophobicity and rigidity (T_g) of the aromatic main chain and the relatively hydrophobic H-bond properties³⁰ of the thiourea moieties to prevent H-bond network destruction. Finally, the **pX-PTU** film displayed higher stress (17.2 MPa) and smaller strain (0.64%) upon fracture than the previous aromatic PTU (12 MPa, 2.4%)²² (Fig. S18), suggesting higher mechanical robustness due to the stronger H-bond nature of X-PTUs (Fig. 2c: *vide supra*).

In light of the high-RI yet transparent optical properties of X-PTU, we further adjusted the thermostability and RI while maintaining high transparency by applying a blending strategy with different PTUs.³¹ We selected **mpPh-PTU** as a blending counterpart because of its higher T_g (175 °C) and RI ($n_D = 1.81$). Each PTU was blended by precipitating the DMF solution into methanol, yielding **pX-PTU/mpPh-PTU** blends with **pX-PTU** molar ratios of $x_{\text{pX-PTU}} = 0.72, 0.49, \text{ and } 0.24$ (Fig. S19–S21). Their DSC thermograms display a single T_g that shifts to higher temperature as $x_{\text{pX-PTU}}$ decreases (Fig. 4a), indicating good miscibility between each PTU with 10–20 nm scale homogeneity.³² To further elucidate their miscibility on a smaller scale, we conducted cross-polarization/magic angle spinning (CP/MAS) ¹³C NMR on the **pX-PTU/mpPh-PTU** blends (Fig. S23–S27). In short, the ¹H spin–lattice relaxation time ($T_{1\rho}$) was determined from two areas, aromatic (*ca.* 150–100 ppm) and

methylene (*ca.* 55–35 ppm) signals, for each composition (Fig. S28). While those $T_{1\rho}$ s did not match perfectly, they shifted proportionally with $x_{\text{pX-PTU}}$, confirming interdomain interactions between **pX-PTU** and **mpPh-PTU** in the blended matrices (Fig. 4b and Table S1). Therefore, although those PTUs were phase-separated on a 3–4 nm scale detectable by CP/MAS NMR measurements, they are miscible on a scale below 20 nm, as indicated by the T_g shifts observed in the DSC results.

The drop-cast **pX-PTU/mpPh-PTU** blend films were visibly transparent and exhibited no aggregation, further confirming the good miscibility of the PTUs (Fig. 5a inset). The UV-vis spectra of the blend films showed good transparency (94–96% T for 1 μm thickness), falling between the values of the individual PTUs regardless of the film thickness (Fig. 5a, Table S2, and Fig. S29–S31). These results demonstrated the bleaching effect with improved near-UV transparency upon increasing $x_{\text{pX-PTU}}$. Their ATR-IR spectra showed a consistent peak shift of the H-bonded N–H vibration modes ($\nu_{\text{N-H}}$ and $2\delta_{\text{N-H}}$) (Fig. S32), indicating the presence of homogeneous H-bond networks even in the blended states without any macroscopic phase separation.

The RI spectra also followed consistent shifts in n_D and ν_D corresponding to the blending ratio (Fig. 5b). In short, the **pX-PTU/mpPh-PTU** blend with higher $x_{\text{pX-PTU}}$ exhibited a lower RI and higher ν_D across the entire visible-light region, aligning well with the empirical RI–Abbe trade-off relationship³³ (Fig. 5c). The extinction coefficient (k , the imaginary part of the complex RI) also decreased with higher $x_{\text{pX-PTU}}$, demonstrating the bleaching effect upon **pX-PTU** introduction (Fig. S33). Summarizing the above, **pX-PTU** was miscible with aromatic PTU on a 10–20 nm scale, and their polymer blends produced transparent films with enhanced thermostability and RI. In particular, entry 3 ($x_{\text{pX-PTU}} = 0.24$; Table S2) showed the best balance of thermal and optical

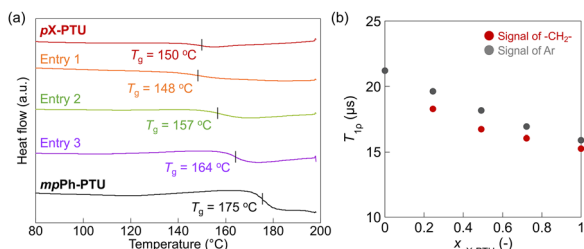


Fig. 4 Miscibility studies of **pX-PTU** and **mpPh-PTU**. (a) DSC thermograms of the blends (2nd heating, scanning rate: 20 °C min^{-1}). (b) Relationship between ¹H spin–lattice relaxation time ($T_{1\rho}$) of the blends measured by solid-state CP-MAS ¹³C NMR and the molar ratio of **pX-PTU** ($x_{\text{pX-PTU}}$).

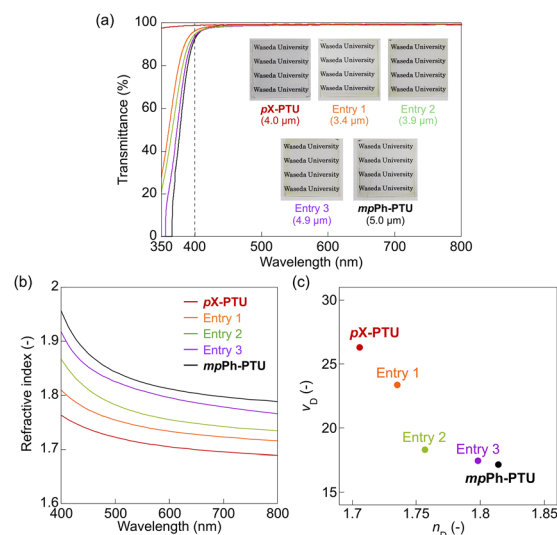


Fig. 5 Optical properties of the films of the **pX-PTU/mpPh-PTU** blends. (a) Normalized UV-vis spectra (film thickness: 1 μm) (inset: photographs and thickness of the films). (b) RI spectra in the visible-light region (for the overall spectra, see Fig. S32). (c) n_D versus ν_D .



properties among the PTU family, exhibiting a high T_g (164 °C) and ultrahigh RI ($n_D = 1.80$), while simultaneously achieving a reasonable Abbe number ($\nu_D = 17$) and visible light transparency (94%T, 1 μm thickness).

In summary, we demonstrated the X-PTU family as an HRIP substructure with unprecedented near-UV-vis transparency and Abbe numbers (e.g., **pX-PTU**: $n_D = 1.71$, $\nu_D = 26$). The key molecular design lies in the “de-conjugated” H-bonds, which involves separating the polarizable aromatic and thiourea moieties with sandwiched methylene spacers to inhibit their orbital interactions while maintaining high polarizability and H-bond density. In particular, **pX-PTU** exhibited adequate thermostability ($T_g = 150$ °C) and good miscibility with **mpPh-PTU** on a 10–20 nm scale, and their blended films demonstrated adjustable thermal and optical properties. To our knowledge, this study is the first to demonstrate how orbital interactions in an HRIP bearing polarizable H-bonds affect the overall optical properties. Furthermore, miscible polymer blending is verified as a simple strategy to adjust the thermal and optical properties. Expanding this concept to diverse polarizable H-bond containing HRIP skeletons (e.g., poly(thioamide)^{23,34} and poly(sulfamide)³⁵) leads to the further design of optical polymers surpassing the empirical RI–Abbe trade-off limit.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI. Supplementary information: Experimental and synthetic procedures, characterization data, computational calculation, solid-state NMR results, and additional properties for the blends. See DOI: <https://doi.org/10.1039/d5cc03785a>.

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