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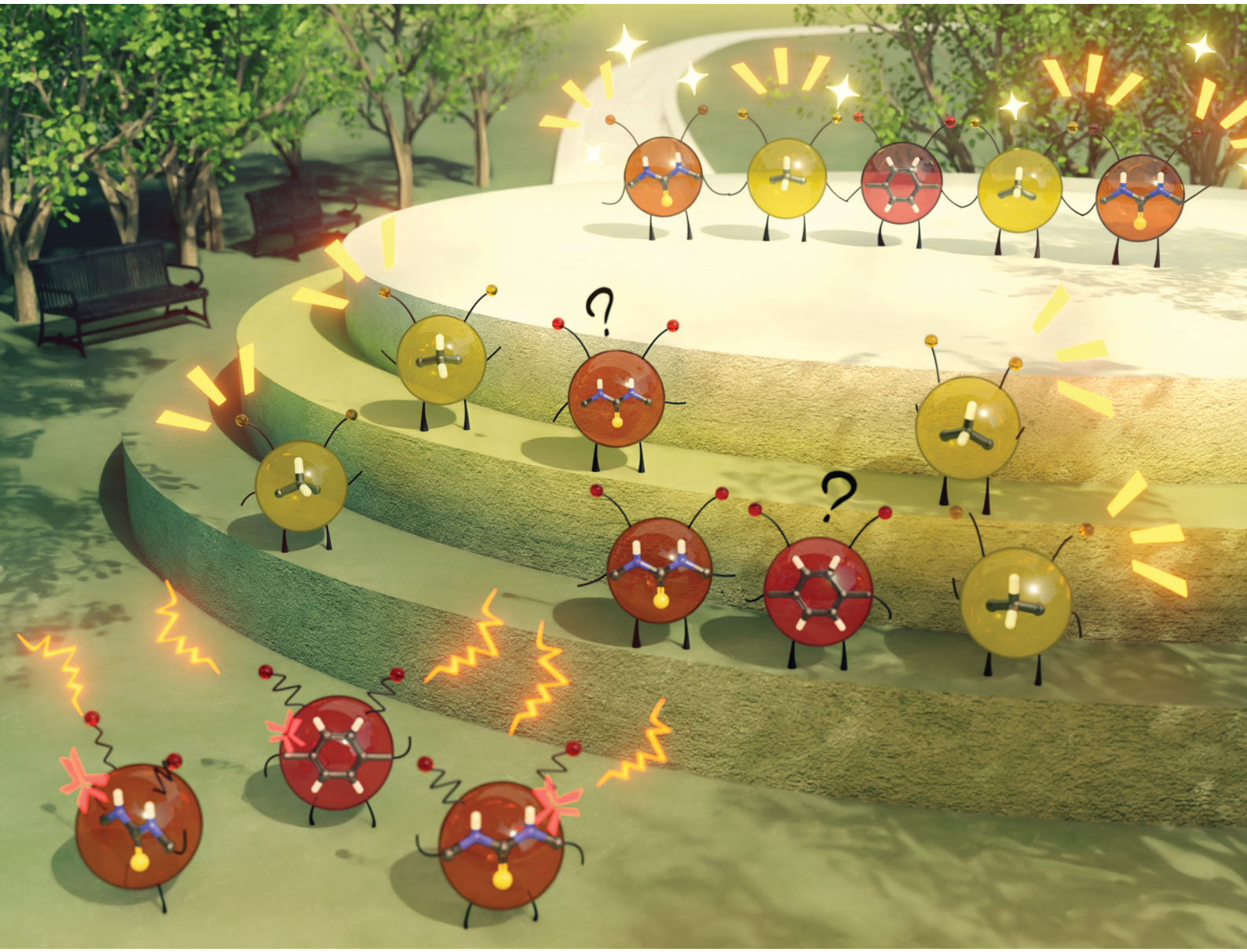

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Bleaching effect of high refractive index xylylic poly(thiourea)s with "de-conjugated" polarizable hydrogen bonds

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Poly(*p*-xylylene thiourea) (*p*X-PTU) exhibits high visible-light transparency (%*T* ≧ 99), a high refractive index (n_D = 1.71), and a reasonable Abbe number (ν_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 *p*X-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 interactions[18]). To address this empirical dilemma, we previously developed hydrogen-bonding (H-bonding) poly(phenylene sulfide)s to achieve both ultrahigh RI (n_D ∼ 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 ∼ 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 (ν_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 (***p*X-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 (ν_D = 26) with its high RI (n_D = 1.71) maintained (Fig. 1, right). In addition, ***p*X-PTU** showed good miscibility with all-aromatic poly(1,3-phenylene-*alt*-1,4-phenylene thiourea) (***mp*Ph-PTU**), producing simply blended transparent films with an enhanced T_g and well-balanced optical properties (T_g = 164 °C, n_D = 1.80, ν_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).

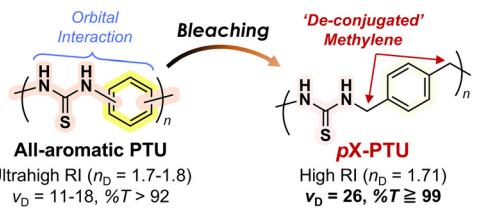

Fig. 1 The concept of "de-conjugated" polarizable H-bonds: from all-aromatic PTU[21] (left: prior work) to ***p*X-PTU** (right: this work) to bleach high-RI PTUs.

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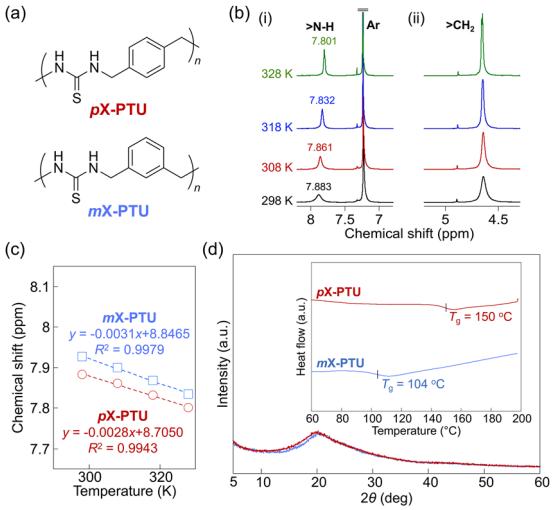

Fig. 2 Properties of X-PTUs. (a) Chemical structures of ***p*X-PTU** and ***m*X-PTU**. (b) ^{1}H VT-NMR of ***p*X-PTU** (i) at 8.2–6.8 ppm (>N–H and aromatic signals) and (ii) at 5.2–4.3 ppm (methylene signals). (c) Temperature dependence of >N–H chemical shifts in ^{1}H VT-NMR. (d) XRD profiles (inset: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

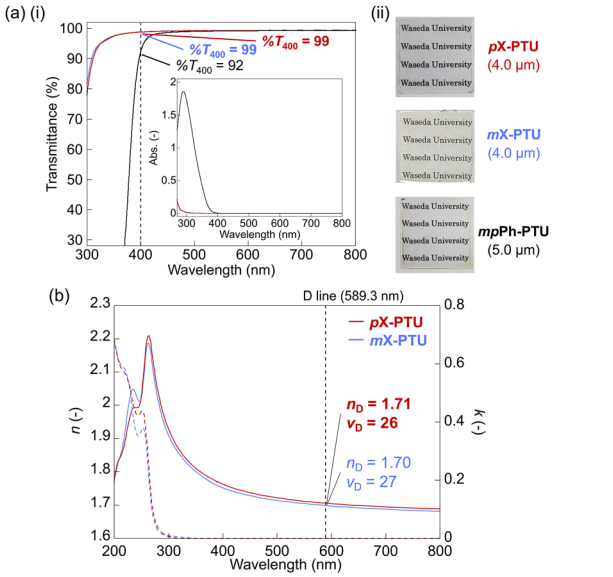

Fig. 3 Optical properties of X-PTUs. (a) (i) Normalized UV-vis spectra for the films (thickness: 1 μm) of X-PTUs and ***mp*Ph-PTU** (inset: UV-vis absorbance spectra of 0.1 mM solution in DMF). (ii) Photographs of PTU thin films on glass substrates and their thickness. (b) RI spectra: *n* (solid line)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

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 ^{1}H and ^{13}C NMR spectroscopy, showing signals of thiourea, aromatic, and methylene groups (Fig. S1–S4). The IR spectra indicate two N–H conformations of thiourea ($\nu_{N-H(trans/trans)}$: ~3270 cm^{-1} and $2\delta_{N-H(cis/trans)}$: ~3055 cm^{-1}), suggesting the presence of randomized H-bond networks (Fig. S5). Upon increasing the temperature, the ^{1}H 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 (-2.8×10^{-3} ppm K^{-1}) than ***m*X-PTU** (-3.1×10^{-3} ppm K^{-1}) and previously reported phenylene-PTUs ($< -3.5 \times 10^{-3}$ 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 °C) and a high pyrolysis temperature (T_{d5} ~ 240–250 °C), significantly surpassing those of phenylene-PTUs (T_g ~ 150 °C, T_{d5} ~ 180 °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 °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.

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 ***mp*Ph-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 ~ 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 (ν_D = 26 (***p*X-PTU**) and 27 (***m*X-PTU**)) compared with those of the reported phenylene-PTUs (ν_D ~ 11–15)[21] and dimethyl-substituted PPS with a similar RI (n_D = 1.69, ν_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 bonds[29] that induced lower transparency and RI (Fig. S12 and S13), the optical properties of ***p*X-PTU** were less deteriorated after the UV treatment than those for ***mp*Ph-PTU**, thanks to the "de-conjugated" xylylene unit with less orbital interactions. In addition, there has been minimal change in RI and transparency of ***p*X-PTU** after the high-temperature or humid exposure (difference of $\%T_{400}$ ~ 1%, n_D ~ ±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 properties[30] of the thiourea moieties to prevent H-bond network destruction. Finally, the ***p*X-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 ***mp*Ph-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 ***p*X-PTU**/***mp*Ph-PTU** blends with ***p*X-PTU** molar ratios of $x_{pX\text{-}PTU}$ = 0.72, 0.49, and 0.24 (Fig. S19–S21). Their DSC thermograms display a single T_g that shifts to higher temperature as $x_{pX\text{-}PTU}$ 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) ^{13}C NMR on the ***p*X-PTU**/***mp*Ph-PTU** blends (Fig. S23–S27). In short, the ^{1}H 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 $x_{pX\text{-}PTU}$, confirming interdomain interactions between ***p*X-PTU** and ***mp*Ph-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 ***p*X-PTU**/***mp*Ph-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 $x_{pX\text{-}PTU}$. Their ATR-IR spectra showed a consistent peak shift of the H-bonded N–H vibration modes (ν_{N-H} and $2\delta_{N-H}$) (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 ***p*X-PTU**/***mp*Ph-PTU** blend with higher $x_{pX\text{-}PTU}$ exhibited a lower RI and higher ν_D across the entire visible-light region, aligning well with the empirical RI–Abbe trade-off relationship[33] (Fig. 5c). The extinction coefficient (k, the imaginary part of the complex RI) also decreased with higher $x_{pX\text{-}PTU}$, demonstrating the bleaching effect upon ***p*X-PTU** introduction (Fig. S33). Summarizing the above, ***p*X-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 ($x_{pX\text{-}PTU}$ = 0.24; Table S2) showed the best balance of thermal and optical

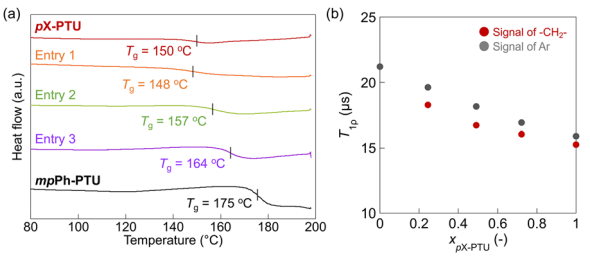

Fig. 4 Miscibility studies of ***p*X-PTU** and ***mp*Ph-PTU**. (a) DSC thermograms of the blends (2nd heating, scanning rate: 20 °C min^{-1}). (b) Relationship between ^{1}H spin–lattice relaxation time ($T_{1\rho}$) of the blends measured by solid-state CP-MAS ^{13}C NMR and the molar ratio of ***p*X-PTU**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

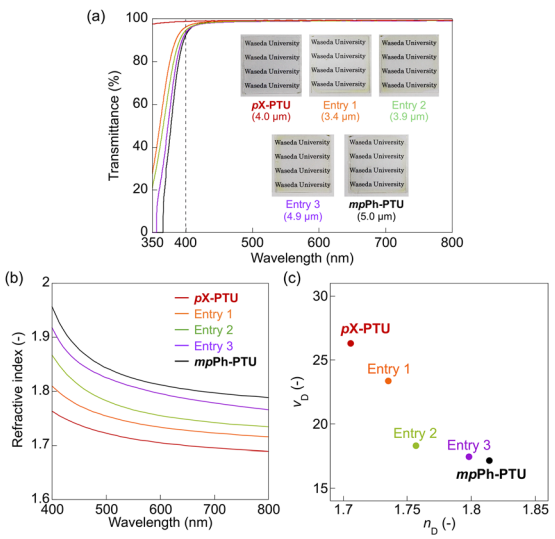

Fig. 5 Optical properties of the films of the ***p*X-PTU**/***mp*Ph-PTU** blends. (a) Normalized UV-vis spectra (film thickness: 1 μm) (inset: photographs and thickness of the films). (b) RI spectra in the visible-light region (for the overall spectra, see Fig. S32). (c) n_D *versus* ν_D.

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 (ν_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.*, ***p*X-PTU**: n_D = 1.71, ν_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, ***p*X-PTU** exhibited adequate thermostability (T_g = 150 °C) and good miscibility with ***mp*Ph-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)s[23,34] and poly(sulfamide)s[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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