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Bioinspired hole-conducting polymers for application in organic light-emitting diodes†Chih-Chia Cheng,^a Yu-Lin Chu,^a Pei-Hsiu Huang,^a Ying-Chieh Yen,^a Chih-Wei Chu,^{bc} Arnold C.-M. Yang,^d Fu-Hsiang Ko,^e Jem-Kun Chen^f and Feng-Chih Chang^{*ag}

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A novel uracil-functionalized poly(3-thiophene) as a hole-injecting/transporting layer in an organic light-emitting device is able to form physical crosslinkages resulting in high thermal stability, non-corrosion, excellent hole injection/transport and electron-blocking capabilities in the solid state, and it achieves up to 10 times higher performance than that of conventional poly(3-thiophene)s under similar experimental conditions.

Organic and polymer light-emitting diodes (OLEDs and PLEDs) based on conjugated polymers have drawn great attention in recent years because of their low power consumption, light weight, rapid response and wide viewing angle.^{1–3} In addition, researchers have witnessed significant progress regarding the brightness, multi- or full-colour emission, and durability and thermal stability of LEDs.^{4,5} One of the most extensively studied conjugated polymers is polythiophene which possesses relatively high chemical stability, easier synthetic accessibility, and potential to be modified at the 3- and 4-ring positions of the thiophene heterocycles to fine-tune the optoelectronic characteristics.^{6,7} Based on the above properties, polythiophenes functionalized in their alkyl chain have been prepared with several applications such as active materials for LEDs.^{8,9}

More recently, research on organic materials possessing low hole-injection and high conductivity has been mainly focused

on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) because of its planar structure which leads to high electron delocalization along the chain, and its relatively high conductivity (10^{-3} to 10^{-5} S cm⁻¹) and good transparency affecting carrier injection and device performance directly.^{10–12} In addition, it has been applied in numerous electronic devices including LEDs,^{13,14} photovoltaic devices,¹⁵ and organic thin-film transistors.¹⁶ However, the residual water in the PEDOT–PSS due to its fabrication process is relatively more destructive than oxygen for organic and polymer LEDs.^{17,18} Efforts to develop novel hole injection/transport materials (HITMs) containing neither ion nor hydrophilic functionality and possessing properties similar or superior to PEDOT:PSS have been actively pursued.

There is an imminent need to find new hole injection materials which are covalently cross-linked HITMs to form solvent-resistant hole-injection layers. Various thermally,^{19–23} photochemically^{24–29} and electrochemically^{30–32} cross-linked materials can overcome the interfacial mixing caused by solution processing, however, additional processes are required. Highly complementary noncovalent bonds (e.g., hydrogen bonds, electrostatic interactions and chain entanglements) leading to a physically cross-linked structure may form covalently cross-linked materials without any additional processes. In previous studies, we have reported the biocomplementary interactions between a nucleobase-like side-chain homopolymer and alkylated nucleobases mediated by thymine–adenine and uracil–adenine base pairs.^{33–35} Recently, we have further developed a new DNA-mimetic π -conjugated poly(triphenylamine-carbazole) (PTC-U) which exhibits amorphous nature, high thermal stability, excellent hole injection and electron-blocking ability in the solid state owing to the uracil induced physical cross-linking. In addition, a trilayer device with PTC-U as a hole injection/transport layer is almost 1.6 times higher than that of the commercial product PEDOT:PSS-based devices.³⁶ There remain many aspects of network-forming clusters transferred from binding and recognition events in fundamental research into non-covalent systems. In this study, new nucleobase-functionalized poly(3-thiophene)s (P3HTs) containing pendant uracil groups have been prepared which exhibit high thermal stability, non-corrosion, solvent resistance, excellent hole injection and electron-blocking abilities in the solid state owing to the uracil induced physical cross-linking. Moreover, when the uracil-containing P3HTs are utilized as a hole-injecting/transporting layer (HITL) in the

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double layer OLED device (anode/HITL/Alq3/cathode), the performance of the resulting device is more than 10 times higher than that of the conventional P3HTs.

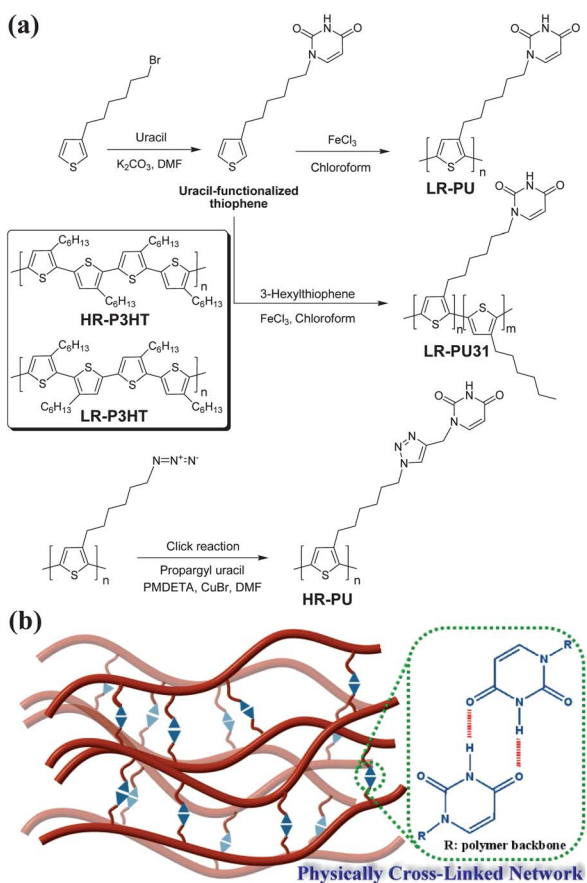
Synthesis of uracil-functionalized P3HTs with different regioregularities

The synthesis of a novel uracil-functionalized thiophene monomer is described in ESI† (Scheme 1a) which was subjected to oxidative polymerization in the presence of FeCl_3 ,³⁷ allowing the preparation of low-regioregular P3HTs containing pendant uracil groups (LR-PU). In order to prepare high-regioregular P3HTs containing pendant uracil groups (HR-PU), it is necessary to synthesize an azide functional P3HT by the Grignard metathesis (GRIM) method,^{38,39} and it was subsequently functionalized by the click reaction with propargyl uracil⁴⁰ to give HR-PU. The structures and reaction pathways of LR-PU and HR-PU are shown in Scheme 1a (detailed synthetic strategy is described in the ESI†). Properties of LR-PU and HR-PU are summarized in Table S1.† Since the electrical responses of LR-PU and HR-PU may be modulated through the intermolecular uracil-uracil (U–U) interaction (Scheme 1b), the self-assembly of these complexes in the bulk state was analyzed using FT-IR spectroscopy as shown in Fig. S5.† The characteristic peaks were those of the free amide NH groups (3475 cm^{-1}) of HR-PU and that involved in U–U (3188 cm^{-1}) interactions as shown in Fig. S5.†^{33,34} Interestingly, the

vibration at 3118 cm^{-1} revealed that the uracil side groups within LR-PU were fully involved in U–U interactions while those of the HR-PU remained disordered with less U–U interactions. This observation indicates that the high-regioregular HR-PU possesses steric hindrance affecting the formation of the intermolecular hydrogen bonds. In addition, the LR-PU was subjected to variable-temperature FT-IR spectroscopic analyses. Based on FTIR spectra obtained at 40 to $180\text{ }^\circ\text{C}$ (Fig. S6†), the U–U interactions between LR-PU chains are extremely stable in the bulk state, which has rarely been observed previously.³³ In order to quantitatively understand the binding affinity of LR-PU, ^1H NMR spectroscopy was employed to determine its association constant (K_a). Since LR-PU is insoluble in nonpolar organic solvents such as CDCl_3 , which is often used in ^1H NMR titration experiments, a low-regioregular P3HT-co-PU copolymer (LR-PU31, uracil content = 33% by weight, see ESI†) was synthesized by the FeCl_3 method in CDCl_3 at $25\text{ }^\circ\text{C}$ for the calculation of the K_a value of the U–U interaction. When the LR-PU31 concentration is systematically increased from 0.56 mM to 2.25 mM, the uracil N–H proton peak is dramatically shifted downfield (8.03 to 8.61 ppm) (Fig. S7†). In addition, the chemical shift of the amide proton of uracil was monitored to give a K_a value of 63.0 M^{-1} from Benesi–Hildebrand plots (Fig. S8†), which is consistent with the K_a values reported previously for U–U interactions.⁴¹

Self-assembly and optical properties of uracil-functionalized P3HTs in the bulk state

Phase behaviors of LR-PU and HR-PU were investigated by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). Fig. 1a presents the WAXD data of the traditional low-regioregular P3HT (LR-P3HT) and the high-regioregular P3HT (HR-P3HT), showing several sharp WAXD peaks due to their crystallinity.^{42–45} The attachment of uracil to the LR-PU and HR-PU side groups leads to the disappearance of these sharp peaks and they are replaced by several amorphous halos at 20.9° , 29.7° , and 40.9° ($d = 0.42$, 0.31 and 0.22 nm , respectively), indicating that the presence of the uracil side groups creates steric hindrance that affect the formation of crystalline P3HT. Moreover, the amorphous halos of



Scheme 1 (a) Synthetic procedures of uracil-functionalized polythiophenes. (b) Graphical representation of the physically cross-linked network formed by uracil-uracil hydrogen bonding interactions.

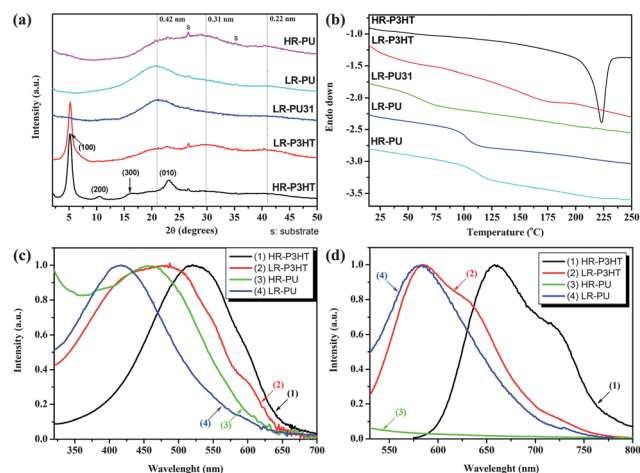


Fig. 1 (a) WAXD data, (b) DSC curves, (c) UV-Vis absorption and (d) PL emission spectra of uracil-functionalized polythiophenes and conventional P3HTs in the solid state.

LR-PU are obviously shifted to lower values of 2θ (0.42 nm) as compared with HR-PU, indicating the formation of a specific structure with relatively larger size.^{33,34} In the DSC curves shown in Fig. 1b, the LR-P3HT and HR-P3HT exhibit melting points (T_m) at 175 and 223 °C, respectively. The glass transition temperatures of LR-P3HT and HR-P3HT appeared at 104 and 114 °C, which can be attributed to the supramolecular binding motif in the bulk playing a critical role in affecting the nature of miscibility between the uracil groups and P3HT chains. To characterize the optical properties of these polymers, the solid state UV-Vis absorption and photoluminescence (PL) emission spectroscopies were employed and the results are shown in Fig. 1c and d. LR-P3HT and HR-P3HT exhibit strong red shifts in their UV-Vis and PL spectra, whereas significant blue-shifts were observed for LR-PU and HR-PU. This observation was due to the lack of pi-stacking^{42,43} and crystal alignment^{44,45} that tend to decrease the inter-chain exciton and the aggregation of the chromophoric backbones was due to the presence of the uracil groups. Notably, the PL spectrum of HR-PU did not show any emission peak, implying that the free uracil groups (Fig. S5†) have the ability to quench excitons in HR-PU. In addition, both LR-PU and HR-PU are able to self-assemble to form a physically cross-linked structure which is potentially applicable in the fabrication of a multilayer polymer LED (PLED) device. High solvent resistance is a prerequisite for a multilayer PLED fabricated by solution processes. The solvent resistance of these polymers to chlorobenzene was investigated *via* UV-Vis spectroscopy (Fig. S9–S12†), and the data showed that the physically cross-linked LR-PU and HR-PU films were completely resistant to chlorobenzene. In contrast, most of the absorptions from LR-P3HT and HR-P3HT films disappeared after the rinsing process. Therefore, the solution-processable and physically cross-linkable characteristics of LR-PU and HR-PU are beneficial for the fabrication of a multilayer PLED device.

Photoluminescence and OLED devices using a single hole-injecting/transporting layer

To assess the charge injection of the polymer, the electrochemical characteristics of LR-PU and HR-PU thin films were investigated through cyclic voltammetry (CV) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the internal standard, and the results are summarized in Fig. 2. The highest occupied molecular orbital (HOMO) levels of these polymers are at *ca.* -5.12 to -5.19 eV, which are very close to the work function of indium tin oxide (ITO) glass (HOMO = -4.9 eV). In

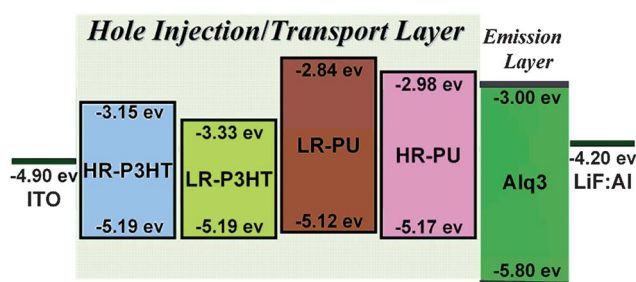


Fig. 2 Configuration and energy level diagram of the double layer organic light-emitting diode. Shown are the highest occupied and lowest unoccupied molecular orbitals of uracil-functionalized polythiophenes and conventional P3HTs.

addition, because the LOMOs of LR-PU and HR-PU are at -2.84 and -2.98 eV, the energy barrier for electron-blocking ability is significantly increased relative to those for LR-P3HT and HR-P3HT. This result demonstrates the critical importance of the presence of uracil groups that can strongly modulate the electrical properties of the conjugated polymers through a specific hydrogen-bonding interaction.⁴⁶ To investigate the hole-injecting/transporting ability of the new materials, an OLED device has been assembled through sequential coating of HITL material, Alq3 (as an emitter layer, EML), LiF (electron injection layer, EIL) and Al (electrode) layers onto ITO (transparent anode) [*i.e.*, ITO/HITL (30 nm)/Alq3 (60 nm)/LiF (1 nm)/Al (100 nm)]. When the LR-PU and HR-PU were used as the HITL, the electroluminescence (EL) spectra of the Alq3 double layer device peaked at 516 nm (Fig. 3a), indicating that these HITMs only serve as hole-transporting materials without causing exciplex formation at the interface with Alq3. In contrast, EL spectra of LR-P3HT and HR-P3HT revealed two maxima at 516 and 628 nm, arising from the emissions from Alq3 and P3HT layers, respectively. Therefore, the LR-PU and HR-PU based devices exhibit a slightly higher operating voltage than the control LR-P3HT and HR-P3HT devices at the same brightness of 1 cd m⁻² (Fig. S13†), which can be attributed to the enlarged energy difference between the redox potentials of these materials (Fig. 2). In other words, the LR-PU and HR-PU can substantially increase the electron-blocking capability of HITLs, leading to a large enhancement of the color stability in green OLEDs. A summary of the display characteristics is shown in Table 1 and Fig. S13–S17,† the maximum external quantum efficiency and power efficiency of the LR-PU-based device are more than 10 times higher than those of LR-P3HT and HR-P3HT devices. In addition, as shown in Table 1, the performance of the LR-PU31-based device is

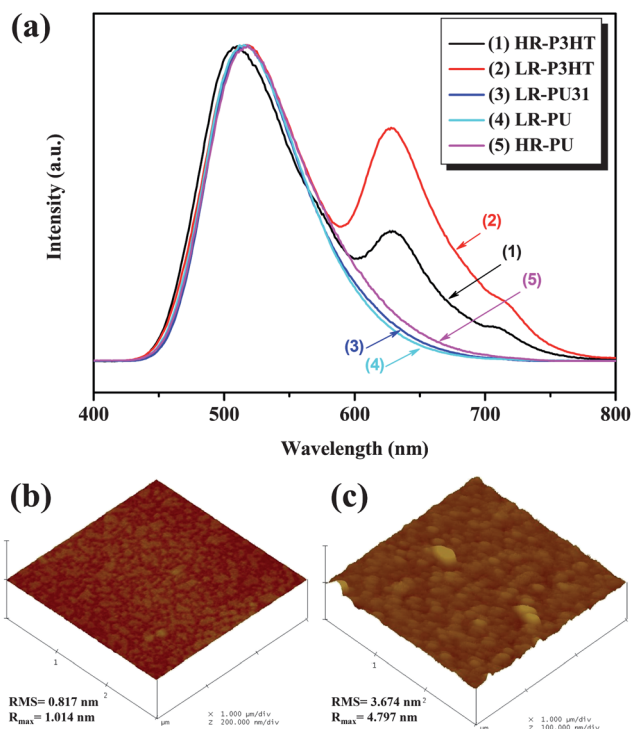


Fig. 3 (a) EL spectra of OLEDs with five different HITLs (HR-P3HT, LR-P3HT, LR-PU31, LR-PU and HR-PU). AFM images of (b) LR-PU and (c) HR-PU thin films as-cast and annealed at 150 °C for 1 h, respectively, on ITO substrates.

Table 1 Electroluminescence of a device based on the structure of ITO/HITLs/Alq3/LiF/Al

HITLs	V_{on}^a (V)	η_{max}^b (%)	LE_{max}^c (cd A^{-1})	ηE_{max}^d (lm W^{-1})	B_{max}^e (cd m^{-2})	VB_{max}^f (V)
HR-P3HT	2.7	0.04	0.041	0.05	1170	10.50
LR-P3HT	3.1	0.07	0.049	0.05	2576	13.50
LR-PU31	3.5	0.13	0.419	0.25	2568	11.02
LR-PU	3.7	0.37	1.245	1.24	6310	11.51
HR-PU	4.3	0.07	0.068	0.09	713	12.00

^a Turn-on voltage. ^b Maximum external quantum efficiency. ^c Maximum luminance efficiency. ^d Maximum power efficiency. ^e Maximum brightness. ^f Driving voltage corresponding to maximum brightness.

relatively lower, indicating that the hole-injection/transport capability increases gradually with increasing uracil content. In the case of the HR-PU-based device with fairly high content of uracil, significantly reduced performance is observed due to the high regioregularity on polymer backbones resulting in a steric effect that hinders the formation of the intermolecular hydrogen bonds. The AFM images (Fig. 3b and c) as well as OLED data reveal that the HR-PU thin film exhibits a spherical morphology with a high root-mean-square (RMS) surface roughness (3.674 nm). In contrast, the LR-PU thin film has a relatively smooth and uniform morphology. The RMS and maximum roughness are *ca.* 0.817 and 1.014 nm, respectively. This result further demonstrated that the LR-PU network serving as a direct pathway for hole transport led to a marked improvement in the performance of the devices. Therefore, the enhanced performance can also be attributed to balanced charge fluxes within the electron-emitting layer (better hole injection, hole transporting and electron-blocking properties) and better thermal stability due to the physically cross-linked structure. Furthermore, it is notable that the performance of the ITO/LR-PU/Alq3/LiF/Al device in terms of maximum brightness (6310 cd m^{-2}) and luminance efficiency (1.245 cd A^{-1}) is very close to the multilayer device of ITO/PEDOT:PSS/Alq3/LiF/Al reported elsewhere,^{47,48} indicating that the physically cross-linked network structure through hydrogen bonds promotes the hole-injecting/transporting and electron-blocking capabilities.

In summary, a series of uracil-functionalized P3HTs with different regioregularities have been developed and characterized. Energy level studies suggest that the uracil units provide suitable HOMO and LUMO for efficient charge extraction and transport. The physically cross-linked LR-PU results in marked enhancement of thermal stability, solvent resistance, surface smoothness, hole injection/transport and electron-blocking ability. In addition, the resulting light-emitting device reaches a maximum brightness of 6310 cd m^{-2} and a luminance efficiency of 1.24 cd A^{-1} which are several times higher than those of conventional OLEDs using conventional LR-P3HT and HR-P3HT as a single HITL. The LEDs fabricated using LR-PU exhibit comparable or even superior performance relative to devices from commercialized PEDOT:PSS. LR-PU is the first example of supramolecular P3HT possessing high hole-injecting/transporting capacity, providing a potential route towards next-generation high efficiency LED devices.

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