Exploiting our recently developed bilayer interface methodology, together with a new wide energy-gap, low LUMO acceptor (A) and the designated donor (D) layers, we succeeded in fabricating an exciplex-based organic light-emitting diode (OLED) systematically tuned from blue to red. Further optimization rendered a record-high blue exciplex OLED with $\eta_{\text{ext}}$ of 8%. We then constructed a device structure configured by two parallel blend layers of mCP/PO-T2T and DTAF/PO-T2T, generating blue and yellow exciplex emission, respectively. The resulting device demonstrates for the first time a tandem, all-exciplex-based white-light OLED (WOLED) with excellent efficiencies $\eta_{\text{ext}}$: 11.6%, $\eta_{\text{c}}$: 27.7 cd A$^{-1}$, and $\eta_{\text{p}}$: 15.8 ml W$^{-1}$ with CIE(0.29, 0.35) and CRI 70.6 that are nearly independent of EL intensity. The tandem architecture and blend-layer D/A (1:5) configuration are two key elements that fully utilize the exciplex delay fluorescence, providing a paragon for the use of low-cost, abundant organic compounds en route to commercial WOLEDs.

Recently, to circumvent the high-cost, limited sources, and potential health threats raised by the transition metal complexes incorporated in organic light emitting diodes (OLEDs), two upconversion mechanisms including triplet-triplet annihilation (TTA) and thermally activated delay-fluorescence (TADF) have been successfully utilized to yield high efficiency OLEDs with tailor-made organic emitters. Particularly, the attainable 100% internal quantum efficiency (IQE) of TADF-based OLEDs has been receiving considerable attention.

A key element for generating efficient TADF lies in the small singlet-triplet energy $D_{\text{ST}}$, i.e., the small electron exchange energy. This can be achieved, in theory, by having orthogonality or slim overlap between HOMO and LUMO involved in the transition. Accordingly, organic molecules capable of demonstrating TADF are composed of structurally weak-coupled electron donor (D) and acceptor (A) components, inducing an intramolecular charge transfer (ICT) behavior. This makes the design of a new D/A molecule to attain efficient TADF a nontrivial matter, one requiring the subtle harnessing of the degree of ICT within the molecular framework. Alternatively, a similar result can be achieved by the formation of exciplex via intermolecular charge transfer between physically blended electronic donor and acceptor molecules. The realization of this simplicity has caused a rapid boom in exciplex applications in OLEDs. With the judicious selection of donor and acceptor materials, OLEDs with exceptionally high electroluminescence (EL) efficiencies have been achieved recently.

While most researchers have utilized a mixed layer for D and A in OLED applications, in a recent contribution, we have seminally demonstrated a record-high ($\eta_{\text{ext}} \sim 7.7\%$) bilayer-type exciplex-based OLED by using a triazene-centered electron-transporting (ET) molecule 3P-T2T as acceptor and a carbazole-based hole-transporting (HT) material TCTA as donor. The large offsets of TCTA/3P-T2T energy levels assist the accumulation of charge carriers at the interfacial region for increasing the carrier recombination probability to give S1 and T1 exciplex excitons, for which the physical interaction and hence weak D/A coupling results in a very small $D_{\text{ST}}$. As a result, efficient thermally activated $T_1 \rightarrow S_1$ reverse intersystem crossing takes place in the interface, generating the exciplex delay fluorescence that serves as a key for the high performance OLED.

In this contribution, we fully extend the unrecognized potential of this bilayer interface technology. By designing a new acceptor and ingeniously selecting donors, we are capable of fabricating the bilayer, exciplex-based OLEDs systematically fine-tuned from blue to red. With this, we then accomplished a great leap by constructing a tandem structure configured by the two parallel blend layers, generating blue and yellow exciplex emissions simultaneously and consequently an all-exciplex, white light organic light-emitting diode (WOLED) with a record high $\eta_{\text{ext}}$ of 11.6%.
To realize the formation of a high-energy exciplex (>2.6 eV), it is essential to have an ET material with a rather low LUMO (HOMO) for the better electron injection (hole-blocking) and high triplet energy to confine the exciplex exciton. Also, this designated ET material should exhibit high electron mobility comparable to the high hole mobility common of HT materials. Recently, triazine-based molecules have emerged as promising ET materials13–15 as well as host materials for Ir-based phosphors16–19. More recently, we have demonstrated a high efficiency yellow exciplex with TCTA as the HT layer and a triazine-based molecule (3P-T2T)21 as the ET layer. To further reduce the LUMO energy and retain the high triplet energy, we herein introduced diphenylphosphine oxide as the electron-withdrawing group as well as the conjugation-blocking group20–22 to make a new ET material PO-T2T (Fig. 1) for this work (see Supplementary online information for synthesis/characterization).

PO-T2T exhibits excellent thermal stability, with a high decomposition temperature (T_d) of 460 °C (5% weight loss) analyzed by thermogravimetric analysis (TGA). No evident glass transition temperature was observed for PO-T2T by differential scanning calorimetry (DSC). In CH_2Cl_2 solution, PO-T2T shows an absorption maximum centered at 272 nm and an emission peak at 405 nm, ascribed to the π-π* transitions of the 1,3,5-triphenyltriazine core (see Supplementary Fig. S1 online). The lowest lying triplet energy (E_T) of PO-T2T was calculated to be 2.99 eV, referring to the highest energy vibronic sub-band of the phosphorescence spectra measured at 77 K (2Me-THF). In addition, one quasi-reversible reduction potential (−1.97 V vs. Fe/Fe^*) of PO-T2T was detected by cyclic voltammetry analysis (see Supplementary Fig. S2 online). This result was used to calculate the LUMO of PO-T2T to be −2.83 eV and the HOMO to be −6.83 eV, with the equation of HOMO = LUMO − E_g.
where $E_g$ is the optical band gap. The physical data of PO-T2T are summarized as Supplementary Table S1 online.

The intensity of exciplex emission relies on the interfacial charge accumulation densities at the donor/acceptor contacts. Hence, high carrier mobilities may play a role in highly efficient exciplex-based OLEDs to improve the electron-hole capture ability at the interface. Here, we employed ambipolar terfluorene (E3) as the charge-generation layer in the Time-of-Flight (TOF) technique to measure the electron mobility of PO-T2T (see Supplementary Fig. S3 online). As a result, high electron mobility is obtained, which lies in the range of $1.7 \times 10^{-3}$ to $4.4 \times 10^{-3}$ cm$^2$/V·s for fields varying from $8.6 \times 10^3$ to $1.2 \times 10^5$ V/cm.

Exciplex emission is caused by the radiative electronic transition from the LUMO of an acceptor to the HOMO of a donor. Hence, an appropriate selection of the donors (with different HOMO levels) combined with PO-T2T to tune the color from blue to red is crucial to proving the concept. Based on the above results, we selected 1,3-di-(N-carbazolyl)benzene mCP ($6.1$ eV for blue, B), 4,4',4'''-triphenylamine TCTA ($5.62$ eV for green, G), 9,9-di-(di-p-tolyl)aminophenyl)fluorine DTAF ($5.31$ eV for yellow, Y), 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane TAPC ($5.3$ eV for orange, O), and N,N'-diphenyl-N,N'-di-[4-[(N,N'-diphenyl-amino)phenyl]benzidine NPnP ($5.16$ eV for red, R), respectively, as donors in the device structure: ITO/poly(ethyl methacrylate) (PEMA)/NPB/mCP/mCP/mCP/mCP/mCP/mCP/PO-T2T/Al. In order to smooth the hole injection to mCP/PO-T2T interfaces and that EL spectra do not correspond to any monomer emission, indicating that it originates from interfacial electron–hole recombination between the donor (HOMO, hole) and acceptor (LUMO, electron) in a form of intermolecular exciplex. This confirms our assumption that exciplex forms at donor/PO-T2T interfaces and that EL spectra can be harnessed by selecting different HOMO levels of the donor.

The low device efficiency in red (device R) deserves further investigation. We first considered the inefficient electron and/or hole injection that impedes the charge collection. To gain insight into the charge transfer dynamics, the femtosecond fluorescence up-conversion technique was applied to probe the early electron/hole transfer dynamics. Upon 380 nm pulse excitation (fwhm $\approx 100$ fs), as shown in Fig. 3a, the upconverted signal monitored at 450 nm reveals two fast single exponential decay components of $0.6$ ps and $4.5$ ps. Note that the $450$ nm emission, which is supposed to arise from NPnPB(donor) or PO-T2T(acceptor) monomer, is not observable in a steady-state manner for device R (Fig. 2a).

The chemical structures of titled donors are depicted in Fig. 1, and relevant schematic energy level diagrams relative to PO-T2T are shown in Supplementary Fig. S4 online. The physical properties of the donors are also shown in Supplementary Fig. S5–6 online. Fig. 2a reveals the EL spectra and CIE coordinates of the devices B, G, Y, O and R OLEDs with the corresponding emission peak wavelengths at about 471, 552, 572, 586, and 657 nm, respectively. Each of the EL spectra does not correspond to any monomer emission, indicating that it originates from interfacial electron–hole recombination between the donor (HOMO, hole) and acceptor (LUMO, electron) in a form of intermolecular exciplex. This confirms our assumption that exciplex forms at donor/PO-T2T interfaces and that EL spectra can be harnessed by selecting different HOMO levels of the donor.

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The lack of monomer

![Figure 3](www.nature.com/scientificreports)

**Figure 3** | **Transient photoluminescence characteristics.** (a) The early dynamics (fluorescence up-conversion) monitored at 450 nm attributed to the monomer emission of either NPnPB or PO-T2T, which is not seen in the steady-state measurement (see Figure 2a, device R). Red solid line depicts the best fitting curve by two single exponential decay components (time constants 0.6 ps and 4.5 ps). $\lambda_{ex} = 380$ nm. (b) The relaxation dynamics of the exciplex emission monitored at 620 nm for device R. The decay was best fitted (green solid line) by two single exponential decay kinetics ($A_1 e^{-t/t_1} + A_2 e^{-t/t_2}$) with $t_1 = (14 \text{ ns})^{-1}$ ($A_1 = 0.91$) and $t_2 = (360 \text{ ns})^{-1}$ ($A_2 = 0.09$).
emission is consistent with the fast photoinduced electron/hole transfer in the NPNPB(donor)/PO-T2T(acceptor) configuration, generating 650 nm exciplex emission. Since the 380 nm photons are absorbed mainly by NPNPB (see Supplementary Fig. S6 online for the corresponding absorption spectra), it is reasonable to ascribe the major (0.6 ps) component to the rate constant of the electron transfer, while that of the hole transfer is (4.5 ps). Fig. 3b reveals the relaxation dynamics of the 650 nm exciplex emission for device R. The decay was best fitted by two-exponential decay kinetics with 14 ns and 360 ns, in which the former is attributed to the fluorescence. The TADF of 360 ns is relatively short compared to that of >µs for exciplex emission commonly observed in the higher energy region. We thus believe that the inferiority of the 650 nm emission for device R is mainly due to relatively low emission yield in the red. The quenching of emission is associated with the operation of the energy gap law, i.e., the high-frequency vibrational quenching and perhaps smaller radiative decay rate constant $k_\text{r}$ in the red ($k_\text{r} \propto \nu^3$ where $\nu$ denotes the emission energy gap in frequency). In an aim to attain efficient electron–hole capture with high probability in the mCP/PO-T2T, we further optimized OLED structures consisting of ITO/PEDOT:PSS (30 nm)/TPAC (20 nm)/mCP (15 nm)/50 mol% mCP:PO-T2T (20 nm)/PO-T2T (45 nm)/Liq (0.5 nm)/Al. As shown in Fig. 4, device B1 featured a relatively low turn-on voltage of 2 V and a maximum brightness of 24600 cd m$^{-2}$ at 1040 mA cm$^{-2}$ (11 V), with CIE coordinates of (0.17, 0.23). The maximum external quantum ($\eta_{\text{ext}}$), current ($\eta_{\text{i}}$), and power efficiencies ($\eta_{\text{p}}$) were 8.0%, 15.5 cd·A$^{-1}$, and 18.4 lm·W$^{-1}$, respectively, which are significantly higher than those of device B (2.8%, 5.4 cd·A$^{-1}$, and 5.1 lm·W$^{-1}$). The $\eta_{\text{ext}}$ value of 8.0% is higher than the limit of $\eta_{\text{ext}}$ in fluorescence-based OLEDs and is superior to the best blue exciplex OLED reported in the literature. The highly efficient exciplex formation at device B1 is attributable to the balanced holes and electrons in the heterojunction. In addition, the mCP:PO-T2T (1 : 1) mixture layer effectively enhances the molecular contact to improve the light-emitting efficiency and hence attain the record high exciplex-based EL efficiencies in blue.

The success of exciplex-based OLEDs fine-tuned from blue to red then encouraged us to explore their pragmatic application en route toward all-exciplex-based WOLEDs. Although this concept has been reported by inserting two blend layers of m-MTDATA:Al(DBM)$_3$, and TPD:Bphen between HTL and ETL, the coexistence of exciplex emissions in two blend layers tends to shift the exciton recombination region to a lower energy side, resulting in very low efficiency (~0.1 cd·A$^{-1}$) and low color stability. To overcome this problem, we made a leap forward by constructing a tandem structure configured by the two parallel blend layers, generating blue and complementary yellow exciplex emissions simultaneously.

The tandem structure was composed of a two individual blend-layer D/A (1 : 1) configuration by a charge generation layer (CGL) configured as: ITO/PEDOT:PSS (30 nm)/TPAC (20 nm)/mCP (15 nm)/mCP:PO-T2T (1 : 1, 20 nm)/PO-T2T (45 nm)/Liq (1 nm)/Al (1 nm)/MoO$_3$ (5 nm)/DTAF (20 nm)/DTAF:PO-T2T (1 : 1, 20 nm)/PO-T2T (50 nm)/Liq (0.5 nm)/Al (100 nm). Fig. 5(a) shows the electronic level configurations of the tandem WOLED (device W), which is based on the CGL of DTAF/MoO$_3$/Al/Liq layers. In this CGL unit, holes and electrons are generated from the DTAF/MoO$_3$ interface. The generated charge carriers are extracted out of the CGL and then injected into the adjacent sub-OLEDs. As shown in Fig. 4, device W displayed a turn-on voltage of 4.0 V, an $L_{\text{max}}$ of 50300 cd·m$^{-2}$ at 24 V (1090 mA cm$^{-2}$), a maximum $\eta_{\text{ext}}$ of 11.6% corresponding to $\eta_{\text{c}}$ of...
27.7 cd·A⁻¹, and ηg of 15.8 lm·W⁻¹. The EL spectra of this white device exhibit distinct blue (mCP:PO-T2T) and yellow (DTAFO:PO-T2T) exciplex emission bands covering wavelengths from 430 to 730 nm, as shown in Fig. 5(b). Due to the broad exciplex emission band, the color-rendering indices (CRI) of device W were calculated to be as high as 70.1–70.6, which are competitive with those of the two-color white OLEDs documented²⁸. In addition, the spectra of device W also demonstrated highly stable chromaticity (CIEx = 0.28 ± 0.29 and CIEY = 0.34 ± 0.36) at different brightnesses (Fig. 5b) and current densities (see Supplementary Fig. S7 online). The tandem architecture with individual emissive units has better color stability and higher efficiency. These superiorities are attributed to the avoidance of the movement of the charge recombination zone and elimination of the energy transfer between blue and yellow emission layers. The performance with a luminance efficiency of 27.7 cd·A⁻¹ and color stable white emission is considered to be a quantum leap forward for all-exciplex-based WOLEDs.

In summary, we have developed a new ET compound PO-T2T possessing a very low LUMO/HOMO (−2.83/−6.83 eV) and have a proof of concept that a panchromatic range of exciplex emission from blue to red can be attained via systematically tuning the HOMO of the HT material. Based on this, we then demonstrate for the first time a tandem, all-exciplex-based white light organic light-emitting diode (WOLED) with excellent performance. Realizing that T3 → S1 thermally activated delay fluorescence should have IQE of 100%, its utilization to achieve efficient white light generation is still lacking at this stage.⁶•²⁷ The tandem architecture and blend layer D/A configuration turned out to be crucial to accounting for the success; otherwise, the electron and hole are too loosely confined to achieve a designated emitting layer. The all-exci-plex-delay-fluorescence based tandem WOLED with ηext as high as 11.6% unveiled here is thus truly unprecedented.

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Author contributions

K.-T.W., S.-W.L. and S.-H.C. conducted the design, synthesis, and characterizations of PO-T2T, W.-Y.H., and G.-C.F. carried out the OLED device fabrication, measurement, and data analysis. P.-T.C. and T.-Y.K. performed PL decay dynamics and provided the necessary consultations during the write-up of the present article.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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