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Organic Optoelectronics

Dynamically Adaptive Characteristics of Resonance Variation for Selectively Enhancing Electrical Performance of Organic Semiconductors**

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Controllably and selectively tuning molecular functions through extensible and universal approaches is always one of the most important and challenging issues for material science. However, because of the intrinsic correlations between the molecular properties, only certain molecular structural strategies and inter-/intra-molecular effects are effective for a particular property without negatively influencing other properties, let alone applications, which is one of the main hindrances for the further development of organic optoelectronics after it has flourished for decades. Since optical and/or electronic processes are involved in all of the organic optoelectronic applications, for example, organic light emitting diodes (OLEDs),[1] organic photovoltaic cells (OPVs),[2] organic field-effect transistors (OFETs),[3] bio-/chemo-/photo-sensors,[4] memories,[5] and lasers,[6] the intrinsic contradiction between the optical and electronic properties of organic conjugates gradually stands out, resulting in bottlenecks in their device performances leaving them far from the rigorous requirements of commercial applications. The situation of host development for phosphorescent OLEDs (PHOLEDs) is one of the most typical embodiments under the demands of balanced optoelectronic properties for reducing operating voltage and improving device efficiencies, taking account of high triplet energy (E_{T1}) for exothermic energy transfer to the guest, suitable frontier molecular orbital (FMO) energy levels for charge injection, and optimal molecular configuration and composition for balanced carrier transportation.[7] The inherent conflict between optical and electrical properties originates from the dependence of optoelectronic properties on molecular structures and frontier orbital distributions and consequently their sensitivity to modification, leading to solutions mainly focused on the static-state molecular properties, such as ambipolar characteristics of donor (D)–acceptor (A) structures. Recently, our group developed several effective strategies, named short-axis linkage,[8] multi-insulating linkage,[9] and indirect linkage,[10] for constructing D–A and D-π-A type host materials with diphenylphospine oxide (DPPO) as the acceptor and realizing excellent device performance, such as ultralow driving voltages (less than 3 V for onset) and high and stable efficiencies.

Nevertheless, the intramolecular interactions, such as forming low-energy charge transfer (CT) states, in complicated D–A systems should be suppressed by insulating linkages but at the cost of reducing electrical activity. Actually, the static-state D–A configuration is inferior in controlling optoelectronic properties owing to its definite bipolar structure and limited variation, requiring more accurate adjustment of the type and ratio of functional groups for balanced electronic performance. Fortunately, in our previous work, a special effect of N−P=O on charge redistribution by resonance variation was observed as a potential approach for the adjustment of electrical characteristics.[11] Resonance structures are proposed to describe delocalized electrons within certain molecules where the bonding cannot be expressed by one single Lewis formula following the valence bond theory. These resonance structures are useful in evaluating the structures of delocalized

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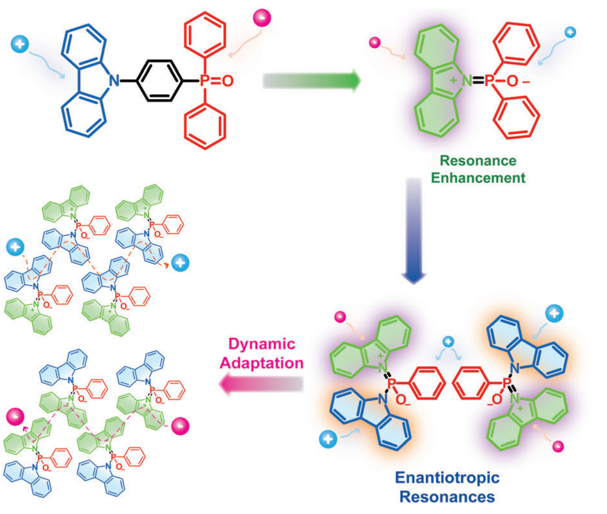
molecules which have a dynamically variable charge distribution.[12] Therefore, the involvement of distinct resonance variation establishes the possibility for regulating molecular electrical properties through new dynamic adaptive processes in real-time, consequently improving the balanced carrier injection and transportation.

Herein the use of resonance variations for the dynamic adaptability of electronic characteristics was systematically investigated on the basis of a series of D–A molecules, namely NCzPO, DNCzPO, NDPhPO, and DNDPhPO containing carbazole or diphenylamine as donor and phenylphosphine oxide (PPO) as acceptor, on the basis of N−P=O resonance (Scheme 1, Figure 1 a, and Supporting Information Scheme S1). N−P=O was formed through the direct linkage of arylamine and PPO moieties. The extremely similar photophysical properties of the mono- and bi-substituted derivatives owing to the insulating P=O groups established the feasibility for selectively modifying electrical properties of the bi-substituted host materials through dynamically adaptive resonance variations. The greater contribution of enantiotropic N$^+$=P−O$^-$ resonances to DNCzPO results in a much enhanced electron transportation from the polarized carbazolyl, accompanied by the preserved hole transportation by the other neutral carbazoly group which is ascribed to the dynamic adaptability of N−P=O for charge transfer by resonance variation. As a result, DNCzPO endowed its blue PhOLED with impressively low driving voltages: 2.6 V for onset, under 3.4 V for 100 cdm^{-2} and under 4.8 V for 1000 cd m^{-2}, as well as favorable electroluminescence (EL) efficiencies, such as a maximum external quantum efficiency (EQE) of up to 16.5 % and power efficiency (PE) > 37 Lm W^{-1}. This work established a solid example for adjusting optoelectronic process through dynamically adaptive behavior and opened the window for purposefully constructing resonance-enhanced D–A systems for diverse optoelectronic applications.



Scheme 1. Schematic drawings of dynamically adaptive characteristics of enantiotropic N−P=O resonances.

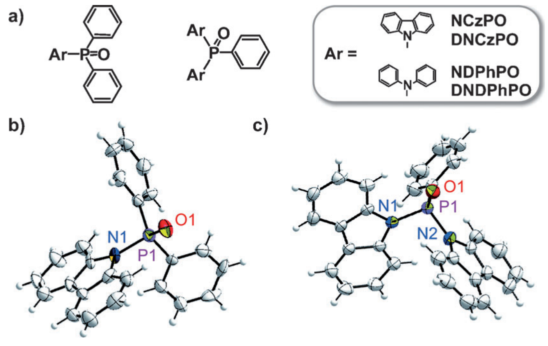


Figure 1. a) structural formula of the arylamine–PO hybrids (left: NCzPO and NDPhPO, right: DNCzPO and DNDPhPO). Single-crystal structures of b) NCzPO and c) DNCzPO.

The shortened N−P bonds in NCzPO and DNCzPO compared with the normal length of 1.76 nm, as indicated by their single-crystal structures, verify the partial double-bond character of N−P through the contribution of N$^+$=P−O$^-$ resonance structures (Figure 1, Table S1 and Table S2). The increased contribution of resonance structures to the dynamic molecular configuration of DNCzPO by its enantiotropic two N$^+$=P−O$^-$ resonance variations is directly evidenced by its shorter N−P bond length. We further investigated the influence of N−P=O resonance on the charge distribution on these charged D–A molecules by Natural Bond Orbital (NBO) calculations (Table S1). With an injected electron, the negative charge is majorly localized on electron-withdrawing PPO unit (71.1 % for NCzPO and 84.6 % for NDPhPO). Significantly, the substantial negative charge, approximately 20 %, distributes on the arylamines. This proportion further increases to up to 33 % when two arylamines are involved in the N$^+$=P−O$^-$ resonance, as for bi-substituted analogues, indicating a more stable contribution of the charge-separated resonance structure N$^+$=P−O$^-$ to the molecular configuration, which is exactly coincident with the shorter N−P bonds found in the single-crystal structures and dramatically modifies the electrical properties of the arylamines favorable for electron injection and transportation. On the contrary, with an injected hole, bi-substitution resulted in the remarkable reduction of the positive charge distribution on PPO, owing to the preservation of one neutral arylamine group in each resonance structure with dominant electron-donating ability (Scheme 1). These results suggest the potential of enantiotropic N$^+$=P−O$^-$ resonances for dynamically balancing carrier exchange between adjacent molecules.

Owing to the insulating characteristic of P=O,[9b] the electronic communication between conjugated groups is effectively suppressed so that the absorption spectra are almost unchanged from monosubstituted to bisubstituted analogues (Figure 2). The electron-withdrawing effect of PPO results in the remarkable hypochromatic shift about 20 nm for the emissions of NCzPO compared with free carbazole (Figure S3 and Table S3). The even larger hypochromatic shift of DNCzPO further reveals its more electron deficient carbazole chromophore with the bigger contributions from N$^+$=P−O$^-$ resonance structures. In films, the absorption spectra are almost unchanged with similar peak wavelengths and profiles, indicating the reduced intermolecular interac-

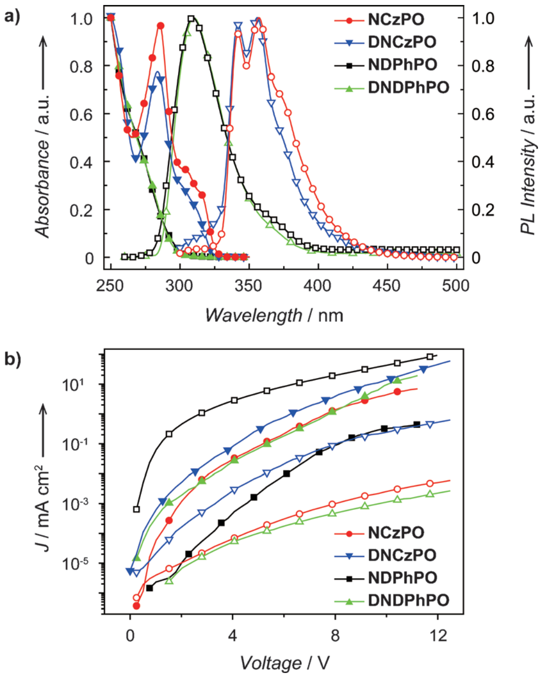


Figure 2. a) Absorption (solid symbols)and fluorescence spectra (open symbols) of the arylamine-PO hybrids in CH_2Cl_2 (10^{-6} mol L^{-1}); b) J/V characteristics of the nominal single-carrier transporting devices based on these arylamine–PO hybrids (solid and open symbols are for electron-only and hole-only devices, respectively).

tions, such as aggregation and π–π stacking (Figure S4). The photoluminescence (PL) spectra of NCzPO and DNCzPO are similar (Figure 2). However, the remarkably reduced vibration bands of bisubstituted DNCzPO testifies to its dynamically enantiotropic resonance configurations, which is further verified by its much lower PL quantum yields (PLQY) than those of NCzPO which suffers from the predominant nonradiative transition by long-term preserved excited energy through stable resonance variations. The spectra of NDPhPO and DNDPhPO showed a similar tendency. The lowest triplet state energy levels (T_1) of these molecules were more than 2.9 eV according to the 0–0 transition bands around 420 nm of the low-temperature time-resolved phosphorescence spectra (Figure S5 and Table S3), which are almost equivalent to those of their chromophores carbazole and diphenylamine[13] owing to the well-controlled T_1 state location at these chromophore as shown by the spin density distribution (Figure S6). Therefore, the optical investigation further confirmed the more stable enantiotropic resonance configurations of bi-substituted analogues accompanied by the similar excited energy levels mainly contributed by their chromophores. This situation provided a flexible platform to study the potential of selectively modulating electrical performance by resonance variations.

The static-state charge-capture ability of these molecules was evaluated according to the energy of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) through a combined theoretical and experimental study using DFT calculations (Figure S7) and cyclic voltammetry (CV) analysis (Figure S8). The HOMOs are dominated by the electron-donating arylamines, giving rise to nearly the same HOMOs with the little variation (experimentally less than 0.07 eV). These HOMOs are lower than that of carbazole (−5.8 eV)[14] owing to the direct linkage with electron-withdrawing P=O. As the opposite effect, arylamines also induce the elevation of the LUMOs compared with that of common phosphine oxide molecules (−2.5 eV)[15] even though the LUMOs are mainly located on PPOs. The separated frontier molecular orbitals (FMOs) of these D–A molecules not only indicate their ambipolar characteristics, but also suggest the great potential of N^+=P–O^- resonance owing to the ability of D and A moieties to stabilize for the positive and negative charges, respectively. It is indicated that in the static state, the direct linkage of D and A seems to weaken their relative electrical capability, which is inconsistent with the actual electrical performance of these D–A molecules and consequently implies the contribution of N^+=P–O^- resonance for dynamic-state charge injection/transportation. The nominal electron-only and hole-only devices were further fabricated to verify the dynamic effect of the N^+=P–O^- resonance on the carrier-transportation (Experiment Section in the Supporting Information). The hole-only current density (J) of NDPhPO is much greater than its electron-only J indicating it has the least stable N^+=P–O^- resonance as a result of the flexible structure of diphenylamine. The much improved stability of the enantiotropic resonance structures of bisubstituted DNDPhPO induced the reversed electrical properties so that the electron transportation became dominant with the electron-only J two orders of magnitude larger than the hole-only value. Owing to the planar and rigid structure of carbazole, the N^+=P–O^- resonance structure of NCzPO is stable enough to support the electron-dominant electrical characteristic. More importantly, DNCzPO exhibited the highest electron-only J, accompanied with the much higher hole-only J compared to NCzPO, resulting in the most balanced carrier transportation among these D–A molecules. The stronger electron transporting ability of the bi-substituted analogues with one more hole-transporting arylamine group showed the direct evidence for the contribution of N^+=P–O^- resonance to the dynamic charge transfer process. Furthermore, the simultaneous improvement of hole and electron transportation in DNCzPO demonstrated the outstanding feature of the enantiotropic resonance variation on dynamic adaptation for the charge transfer (Scheme 1), which undoubtedly establishes a new approach for controllable modulation of optoelectronic properties for organic semiconductors.

To confirm the superiority of resonance-variable materials in optoelectronic devices, especially their dynamic adaptability in electrical processes, the blue-emitting PhOLED devices of NCzPO, NDPhPO, DNCzPO, and DNDPhPO (hosts) based on FIrpic (guest), termed devices **A**–**D**, respectively, were fabricated with the configuration of ITO/MoO_x (2 nm)/m-MTDATA:MoO_x (15 wt %, 30 nm)/m-MTDATA (10 nm)/[Ir(ppz)$_3$](10 nm)/Host: FIrpic (10 nm, 10 %)/BPhen (20 nm)/LiF (1 nm)/Al (100 nm) (Scheme S3).[16] Device **E** based on the conventional host *N*,*N*-dicarbazolyl-3,5-benzene (*m*CP) for blue PHOLEDs were also fabricated for comparison. The turn-on voltages of **A**--**D** were similar to that of **E**, attributed

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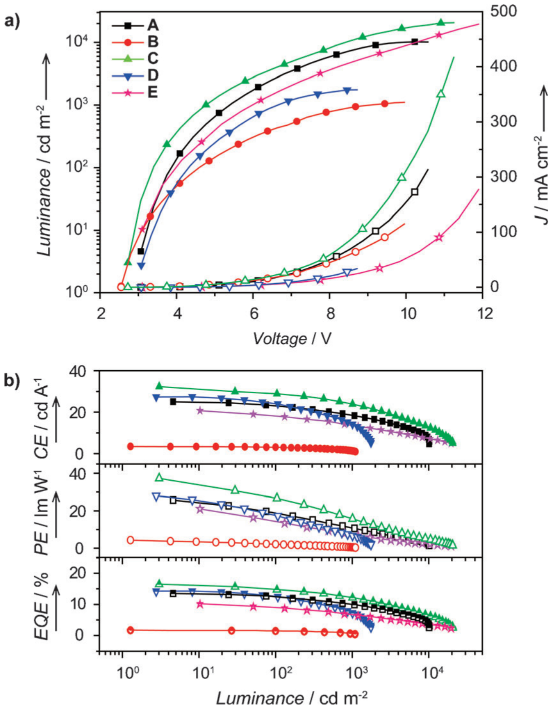

Figure 3. a) Current density (*J*) (open) luminance (solid) voltage curves of devices **A**–**E**; b) Efficiencies–luminance curves of devices **A**–**E**.

to the FMOs of these D–A molecules which are approximately equal to those of mCP (Figure 3 and Table SI4). However, at 100 and 1000 cd m^{-2}, the driving voltages of devices **A, C**, and **D** turned to be about 0.7 and 1.4 V lower than those of **E**, which indicated the effect of the resonance-enhanced carrier transportation compared with *m*CP. In accord with the results of single-carrier transporting devices, DNCzPO endowed **C** with the lowest driving voltages, less than 3.4 V and 4.8 V at 100 and 1000 cd m^{-2}, which were 0.6 and 0.7 V lower than those of **A** and should be ascribed to the dynamically adaptive carrier transportation by its enantiotropic resonance structures during device operation. The driving voltage of less than 4.0 V of **C** at 200 cd m^{-2} makes its application in portable displayers driven by low-voltage power sources feasible.[10a] The small overlap between the emission of NDPhPO and the metal-to-ligand charge-transfer (MLCT) absorption band of FIrpic, its low resonance stability, and the recombination zone close to BPhen with a low E_{T1} of 2.6 eV should be the main reasons for the lowest efficiencies of **B**.[17] Therefore, the stabilized N$^+$=P–O$^-$ resonance of DNDPhPO gives its corresponding device **D** significantly improved maximum efficiencies of 27.4 cd A^{-1} for current efficiency (CE), 28 Lm W^{-1} for power efficiency (PE), and 14.3 % for external quantum efficiency (EQE), which were better than those of **E** (20 cd A^{-1}, 22.7 Lm W^{-1}, and 10.2 %). Nevertheless, the sharply reduced efficiencies of **D** at high luminance still indicated the worse stability of charged DNDPhPO arising from its flexible configuration. NCzPO which has a more stable resonance structure endowed **A** with a much reduced efficiency roll-off of 8.1 % for EQE at 100 cd m^{-2}, accompanied with the comparable maximum efficiencies of 26.0 cd A^{-1}, 26.2 Lm W^{-1}, and 13.5 %. The more balanced carrier transportation in DNCzPO further gave rise to the highest maximum efficiencies of **C** as 32.3 cd A^{-1}, 37.2 Lm W^{-1}, and 16.5 %, which were more than 1.5 fold that of *m*CP-based **E**. The efficiencies of **C** were also rather stable in that at 100 cd m^{-2} the efficiencies of **C** only slightly decreased to 28.9 cd A^{-1}, 23.4 Lm W^{-1}, and 14.7 %, while at 1000 cd m^{-2} the efficiencies still remained as high as 23.4 cd A^{-1}, 15.8 Lm W^{-1}, and 12.2 %, respectively. It is shown that the efficiency stability of these devices is in accord with the resonance stability of their hosts. Since the optical properties of these D–A molecules are similar, the superior EL performance of **C** should originated from the excellent dynamically adaptive electrical performance of DNCzPO provided by its stable enantiotropic resonance variation.

In summary, the selective modulation of electrical properties by the resonance variation and its dynamically adaptive characteristics in charge-transfer process are demonstrated by the bisubstituted carbazole-PO hybrid DNCzPO. On the basis of preserved optical properties inherited from the chromophores by the insulating linkage of P=O, the electron transporting ability of DNCzPO is selectively and greatly enhanced by its N$^+$=P–O$^-$ resonance. This is accompanied by the preserved hole transporting ability of the remaining neutral carbazolyl, which profits from dynamic adaptability of the enantiotropic resonance variation during the electrical processes. As a result, DNCzPO provided its FIrpic-based device with driving voltages as low as 2.6 V for onset, under 3.4 V for 100 cd m^{-2}, and under 4.8 V for 1000 cd m^{-2} for portable applications, and high and stable efficiencies with the maxima of 32.3 cd A^{-1} for CE, 37.2 Lm W^{-1} for PE, and 16.5 % for EQE, which are among the best results of low-voltage-driving blue PHOLEDs reported to date. Benefiting from the flexibility in manipulating electronic structures and properties by resonance variation, this work not only established a new approach for selective modulation of optoelectronic properties for organic semiconductors in dynamic processes, but also further stimulates the new concepts and applications for resonance structured D–A materials.

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