Phenyl-triggered photophysical switching between normal fluorescence and delayed fluorescence in phthalonitrile-based luminophores

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Abstract
Herein, a facile strategy for switching luminescent properties between normal fluorescence and thermally activated delayed fluorescence (TADF) is presented. Two luminophoric molecules, VPN-Ph and VPN-H, combining phthalonitrile as an electron-accepting core and triphenylamines as electron-donating peripheries with and without two phenyl groups, are newly developed. A comparative study on their structural and photophysical properties is conducted. While non-phenyl VPN-H does not exhibit TADF but normal fluorescence, phenyl-introduced VPN-Ph exhibits TADF with a high photoluminescence quantum yield as a consequence of the phenyl-triggered steric congestion. By virtue of the TADF feature, an organic light-emitting diode (OLED) incorporating VPN-Ph as an emitter achieves a maximum external electroluminescence (EL) quantum efficiency as high as 28.0%, which is five times higher than that of the VPN-H-based OLED. Thus, phenyl-triggered geometric modulation has a drastic impact on the resulting photophysical and EL properties, leading to TADF on/off switching.

KEYWORDS
intramolecular charge transfer, molecular orientation, organic light-emitting diodes, photophysical switching, phthalonitrile, thermally activated delayed fluorescence

As third-generation emitters for organic light-emitting diodes (OLEDs), thermally activated delayed fluorescence (TADF) materials have been developed since 2012[1-3] and have attracted growing interest owing to their capability of achieving 100% internal electroluminescence (EL) quantum efficiency (ηint) without the use of precious-metal elements.[4-8] Compared with first-generation fluorescence materials, a remarkable feature of TADF is up-conversion of excitons from the lowest excited triplet (T1) to singlet (S1) states for harvesting both singlet and triplet excitons. In the design of TADF materials, to accelerate the reverse intersystem crossing (RISC) from the T1 to singlet (S1) states for harvesting both singlet and triplet excitons. In the design of TADF materials, to accelerate the reverse intersystem crossing (RISC) from the T1 to singlet (S1) states and thereby enhance delayed fluorescence properties, the energy gap between the S1 and T1 states (∆E_ST) should be minimized in accordance with the relationship k_{RISC} \propto \exp(-\Delta E_{ST}/k_BT), where k_{RISC}, k_B, and T are the RISC rate constant, Boltzmann constant, and absolute temperature, respectively. Because ∆E_ST predominantly depends on the electron exchange energy, most organic TADF materials have been designed by adopting electronic donor–acceptor (D–A) systems possessing intramolecular charge transfer (ICT) characteristics to minimize the overlap integral (I_{H/L}) between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).[4-8] By enlarging the dihedral angle between the D–A planes, the resulting I_{H/L} can be reduced to attain a smaller ΔE_ST. However, lowering ΔE_ST by reducing I_{H/L} in TADF materials inevitably causes a substantial reduction in the oscillator strength (f), which consequently reduces the radiative decay rate constant (k_r) from S1 to the ground state (S0), resulting in a lower photoluminescence (PL) quantum yield (Φ_{PL}). Therefore, to overcome such contradictory prerequisites and attain ideal TADF properties, careful selection of the D–A combinations and precise control of the D–A geometry are crucial.[10,11]

In this paper, we report a photophysical switching between normal fluorescence and TADF triggered by the steric congestion caused by the phenyl substituents, the concept of which is illustrated in Figure 1. VPN-H, which combines a
phthalonitrile (VPN) acceptor core \[12\] and triphenylamine (TPA) donor peripheries, exhibits green normal fluorescence. Remarkably, for VPN-Ph, the introduction of two additional phenyl groups enables the luminophore to turn on the TADF properties through a subtle change in the dihedral angle between the D–A planes. Consequently, OLEDs based on VPN-Ph achieved a notably high maximum external EL quantum efficiency \((\eta_{\text{ext}})\) of 28.0%, which was five times higher than that of the corresponding VPN-H-based devices.

VPN-H was readily prepared via Suzuki–Miyaura cross coupling between 4,5-dichlorophthalonitrile and (4-(diphenylamino)phenyl)boronic acid, whereas VPN-Ph was synthesized via the Buchwald–Hartwig amination of a dibrominated derivative of 3,4,5,6-tetraphenylphthalonitrile with diphenylamine, according to our previously reported synthetic protocol.\[12\] Their detailed synthesis procedures and characterization data are provided in the Supporting Information.

To understand how two additional phenyl substituents affect the geometric and electronic characteristics at the molecular level, we performed density functional theory (DFT) calculations for VPN-H and VPN-Ph at the PBE0/6-31G(d) level (Figure 2). The adiabatic \(S_1\) and \(T_1\) energies \((E_S\) and \(E_T\), respectively), \(\Delta E_{ST}\), and associated \(f\) values were computed using the optimized structures with time-dependent DFT (TDDFT) at the same level. For both molecules, the calculated \(S_1\) and \(T_1\) states were predominated by the HOMO \(\rightarrow\) LUMO transition characterized by ICT. As expected, VPN-Ph exhibited a smaller HOMO/LUMO overlap integral\[13\] \((I_{\text{H/L}} = 33\%)\) than VPN-H \((I_{\text{H/L}} = 42\%)\) because VPN-Ph adopted a more twisted D–A geometry with a larger dihedral angle \((\theta_{\text{D–A}})\) of 62°, stemming from the additional phenyl groups. Consequently, VPN-Ph exhibited larger calculated \(E_S\) and \(E_T\) values (2.62 and 2.04 eV, respectively) and smaller \(\Delta E_{ST}\) (0.46 eV) compared to those of VPN-H. The difference in geometric structures of VPN-H and VPN-Ph was further evidenced by X-ray crystallographic analysis (Figure 2); VPN-Ph showed a larger \(\theta_{\text{D–A}}\) of 71–72° in comparison with VPN-H \((\theta_{\text{D–A}} = 40–48°)\), which is reasonably consistent with the computational results.

Figure 3 depicts the UV–vis absorption and PL spectra of VPN-H and VPN-Ph in toluene solutions. Both compounds
exhibited intense absorption bands around 300 nm, which can be assigned to the locally excited $\pi-\pi^*$ transitions of the respective donor and acceptor moieties. In addition, lower energy broad absorptions originating from the ICT transitions were observed in the range of 350–450 nm, with maximum molar absorption coefficients ($\epsilon_{\text{max}}$) of $1.8 \times 10^4$ and $0.7 \times 10^4$ M$^{-1}$ cm$^{-1}$ for VPN-H and VPN-Ph, respectively. As for the ICT absorptions, the experimental oscillator strength ($f_{\text{exp}}$) was estimated to be 0.26 for VPN-H and 0.10 for VPN-Ph using the relation $f_{\text{exp}} = 4.3 \times 10^{-9} \epsilon_{\text{max}} \Delta \nu_{1/2}$ ($\Delta \nu_{1/2}$: full width at half maximum of the absorption band) $[9]$ roughly agreeing with the calculated $f$ values. VPN-H emitted intense blue-green PL with an emission peak ($\lambda_{\text{PL}}$) at 495 nm, whereas VPN-Ph exhibited a slightly blue-shifted $\lambda_{\text{PL}}$ at 482 nm. Despite the difference in the $f$ values for ICT, VPN-H and VPN-Ph showed comparable absolute $\Phi_{\text{PL}}$ values as high as 93% and 97%, respectively, in deoxygenated toluene solutions. The $\Delta E_{\text{ST}}$ values for VPN-H and VPN-Ph were experimentally determined to be 0.28 and 0.14 eV, respectively, from their room-temperature fluorescence (300 K) and low-temperature phosphorescence (77 K) spectra.

The solid-state photophysical properties of VPN-H and VPN-Ph were further investigated by doping these emitters in 2,8-bis(diphenylphosphinyl)dibenzo]-$[c,f]$furan$[$14$]$ (PPF, $E_T = 3.1$ eV) host matrices, and the corresponding photophysical data are summarized in Table 1. As presented in Figure 4a and b, the doped films of VPN-H and VPN-Ph exhibited bright green PL with $\lambda_{\text{PL}}$ at 525 and 504 nm and $\Phi_{\text{PL}}$ of 86% and 98%, respectively. We also examined the transient PL characteristics of both materials in the doped films (Figure 4c). VPN-H only exhibited normal fluorescence with an emission lifetime ($\tau_p$) of 15 ns; VPN-Ph exhibited distinct two-component emissions involving prompt fluorescence with a similar $\tau_p$ (14 ns) and delayed fluorescence with a lifetime ($\tau_d$) of 440 $\mu$s at 300 K. For the VPN-Ph-doped film, the delayed fluorescence component gradually intensified as the temperature increased from 100 to 300 K, manifesting a typical TADF behavior.

We also examined the photophysical properties of VPN-H and VPN-Ph in their pure neat films (Supporting Information). Notably, both VPN-H and VPN-Ph neat films retained high overall $\Phi_{\text{PL}}$ values of 71% and 66%, respectively. However, for the VPN-Ph neat film, the delayed fluorescence component tended to diminish, and its fractional quantum yield ($\Phi_d = 5\%$) evidentially decreased compared to that of the doped film ($\Phi_d = 26\%$, Figure 4b). This is because relatively long-lived triplet excitons can undergo aggregation-caused quenching through the Dexter energy transfer between the neighboring VPN-Ph molecules in the condensed state. $[15]$

To unveil the effect of phenyl substitution on EL performance, multilayer OLEDs incorporating VPN-H and VPN-Ph as emitters (devices A and B, respectively) were fabricated and evaluated. As illustrated in Figure 5a, the device structure was indium tin oxide (ITO) (110 nm)/4,4′-bis[N-(1-naphthyl)-N-phenylaminol]-1,1′-biphenyl (α-NPD) (40 nm)/1,3-bis(carbazol-9-yl)benzene (mCP) (10 nm)/LiF (1.0 nm)/Al (100 nm). Figure 5b and c depicts the current density–voltage–luminance ($J$–$V$–$L$) and $\eta_{\text{ext}}$–$L$ characteristics.
respectively, while Table 2 presents the main EL data. Evidently, device B using VPN-Ph achieved significantly high EL performance with a maximum $\eta_{\text{ext}}$ of 28.0%, current efficiency ($\eta_c$) of 86.8 cd A$^{-1}$, and power efficiency ($\eta_p$) of 74.0 lm W$^{-1}$, outperforming device A using VPN-H ($\eta_{\text{ext}} = 5.6\%, \eta_c = 18.5 \text{ cd A}^{-1}, \eta_p = 8.7 \text{ lm W}^{-1}$), owing to the TADF feature of VPN-Ph. For device A, the $\eta_{\text{ext}}$ values significantly decreased with increasing current density (or luminance), which should originate from triplet exciton quenching such as triplet–triplet annihilation (TTA) and triplet–polaron annihilation (TPA) owing to the long emission lifetime of VPN-Ph ($\tau_d = 440 \mu$s) in the doped film.$^{[16]}$

We also fabricated OLEDs (devices C and D) using 50 wt%–VPN-Ph:PPF doped and nondoped VPN-Ph neat films as the emission layer (EML), respectively, with the same device configurations (Supporting Information). While device C with the heavily doped EML exhibited a maximum $\eta_{\text{ext}}$ as high as 19.5%, device D with the nondoped EML showed a much lower maximum $\eta_{\text{ext}}$ of 7.2% due to the detrimental triplet exciton quenching in the neat film.

By assuming that the holes and electrons are fully balanced and recombined to form excitons at the EML, the theoretical $\eta_{\text{int}}$ and $\eta_{\text{ext}}$ of OLEDs are given by the following equations$^{[1,2]}$

$$\eta_{\text{int}} = \eta_S \times \Phi_p + \eta_S \times \Phi_d + \eta_T \times \Phi_d / \Phi_{\text{ISC}}$$  \hspace{1cm} (1)

$$\eta_{\text{ext}} = \eta_{\text{int}} \times \eta_{\text{out}}$$  \hspace{1cm} (2)

where $\eta_S$ and $\eta_T$ denote exciton production rates in the singlet and triplet states (25% and 75%, respectively), $\Phi_p$ and $\Phi_d$ are the fractional quantum efficiencies of the prompt and delayed components, respectively ($\Phi_p = 86\%$ and $\Phi_d = 0\%$ for VPN-H; $\Phi_p = 72\%$ and $\Phi_d = 26\%$ for VPN-Ph), $\Phi_{\text{ISC}}$ is the intersystem crossing efficiency ($\Phi_{\text{ISC}} = 1 - \Phi_p$), and $\eta_{\text{out}}$ table 2 presents the main EL data. Evidently, device B using VPN-Ph achieved significantly high EL performance with a maximum $\eta_{\text{ext}}$ of 28.0%, current efficiency ($\eta_c$) of 86.8 cd A$^{-1}$, and power efficiency ($\eta_p$) of 74.0 lm W$^{-1}$, outperforming device A using VPN-H ($\eta_{\text{ext}} = 5.6\%, \eta_c = 18.5 \text{ cd A}^{-1}, \eta_p = 8.7 \text{ lm W}^{-1}$), owing to the TADF feature of VPN-Ph. For device A, the $\eta_{\text{ext}}$ values significantly decreased with increasing current density (or luminance), which should originate from triplet exciton quenching such as triplet–triplet annihilation (TTA) and triplet–polaron annihilation (TPA) owing to the long emission lifetime of VPN-Ph ($\tau_d = 440 \mu$s) in the doped film.$^{[16]}$

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$$\eta_{\text{int}} = \eta_S \times \Phi_p + \eta_S \times \Phi_d + \eta_T \times \Phi_d / \Phi_{\text{ISC}}$$  \hspace{1cm} (1)

$$\eta_{\text{ext}} = \eta_{\text{int}} \times \eta_{\text{out}}$$  \hspace{1cm} (2)

where $\eta_S$ and $\eta_T$ denote exciton production rates in the singlet and triplet states (25% and 75%, respectively), $\Phi_p$ and $\Phi_d$ are the fractional quantum efficiencies of the prompt and delayed components, respectively ($\Phi_p = 86\%$ and $\Phi_d = 0\%$ for VPN-H; $\Phi_p = 72\%$ and $\Phi_d = 26\%$ for VPN-Ph), $\Phi_{\text{ISC}}$ is the intersystem crossing efficiency ($\Phi_{\text{ISC}} = 1 - \Phi_p$), and $\eta_{\text{out}}$
is the light outcoupling efficiency. Accordingly, the theoretically maxima of $\eta_{\text{out}}$ for devices A and B were estimated to be $\sim 22\%$ and $\sim 94\%$, respectively. Given the experimental maximum $\eta_{\text{ext}}$ (Table 2), the $\eta_{\text{out}}$ values for devices A and B were deduced to be $\sim 26\%$ and $\sim 30\%$, which appeared to be higher than the typical value (17) for conventional OLEDs. To clarify the origin of the enhanced $\eta_{\text{out}}$ for devices A and B, we further investigated the orientation behavior of the transition dipole moments for the VPN-H and VPN-Ph-doped films using angle-dependent p-polarized PL spectroscopy. As shown in Figure 6a, the experimental angle-dependent PL data fitted well with models assuming horizontal-to-vertical dipole ratios of 0.82:0.18 for VPN-H and 0.85:0.15 for VPN-Ph, indicating the preferential horizontal orientation of the transition dipole moments relative to the substrate within the EML. As illustrated in Figure 6b, it is found that the transition dipole moments of both VPN-H and VPN-Ph tend to lie nearly parallel to the VPN plane even though there is a certain conformational fluctuation. Thus, the discotic molecular geometries (particularly for VPN-Ph) can induce the anisotropic orientation of the emitters, contributing to the enhancement of $\eta_{\text{out}}$ and thus improving output EL efficiencies.

In summary, we demonstrated a strategy for phenyl-triggered photophysical switching between normal fluorescence and TADF using phthalonitrile-based luminophores. The structural and physicochemical properties and resulting OLED performances were systematically investigated for VPN-H and VPN-Ph, and the phenyl substitution on the phthalonitrile core was found to be responsible for lowering $\Delta E_{\text{ST}}$ and thereby inducing TADF. Consequently, the VPN-Ph-based OLED achieved notably high EL performance with $\eta_{\text{ext}}$ of 28.0%, which was five times higher than that of the VPN-H-based OLED ($\eta_{\text{ext}} = 5.6\%$), despite the similar chemical structure. The present design concept for TADF on/off switching opens up a new avenue for developing attractive organic luminophores with tunable optical and optoelectronic functions.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION
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