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Authors: Ming-De Li, Sirui Yang, Chen Cao, Amjad Islam, Shanshan Sun, Ziqi Deng, Jiayu Li, Shaofei Ni, and Qingxiao Tong

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Multiple Disentangling Effects on Excited State Intramolecular Charge Transfer Among Asymmetrical Tripartite PPI-TPA/PCz Triads

Sirui Yang,^[a] Chen Cao,^{[a],[b]} Amjad Islam,^[a] Shanshan Sun,^[a] Ziqi Deng,^[a] Jiayu Li,^[a] Shaofei Ni,^[a] Qing-Xiao Tong,^{*[a]} and Ming-De Li^{*[a]}

Dedication ((optional))

[a] Sirui Yang, Chen Cao, Dr. Amjad Islam, Shanshan Sun, Ziqi Deng, Jiayu Li, Dr. Shaofei Ni, Prof. Qing-Xiao Tong, Prof. Ming-De Li Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structure Materials of Guangdong Providence, Shantou University, Shantou 515063, China E-mail: qxtong@stu.edu.cn, mdli@stu.edu.cn

[b] Chen Cao

Center of Super-Diamond and Advanced Films (COSDAF), Department of Chemistry, City University of Hong Kong, Hong Kong SAR 999077, P. R. China

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Abstract: Bv utilizing the bipolarity of 1,2diphenylphenanthroimidazole (PPI), two types of asymmetrical tripartite triads (PPI-TPA and PPI-PCz) have been designed with triphenylamine (TPA) and 9-phenyl-carbazole (PCz), respectively. These triads are the deep-blue luminescent materials with a high fluorescence quantum yield of nearly 100%. To trace the photophysical behaviors of these novel triads, the excited states evolution channels and interchromophoric interactions of these triads were investigated by ultrafast time-resolved transient absorption and excited states theoretical calculations. The results suggest that the electronic nature of moieties, asymmetrical tripartite structure and the distance of electron-hole of these triads as well as the polarity of solvent determine the lifetime of intramolecular charge transfer (ICT). Interestingly, PPI-PCz triads demonstrate an anti-Kasha's ICT, the charge transfer direction among the triads is adjustable. For PPI-TPA triad, the electron is transferred from TPA to PPI, while for PPI-PCz triads, the electron is pushed from PPI into PCz mojety. The exploration on the excited state ICT among these triads may pave the way to design a better luminescent material in the future.

Introduction

The organic lighting-emitting device (OLED) technology was first developed in 1987.1 OLED material have diverse prevailing advantages, including; high power efficiency, 2-3 mechanical applicability with flexible devices,⁴ lower cost and environmental protection.⁵ Therefore, OLED is in a dominant position among different types of technologies, such as; smart home devices, flat displays and fluorescent materials over a couple of decades.⁶⁻⁷ To date, abundant typical tricolor molecular materials have been synthesized to fabricate full-color OLED displays,8-9 while some issues related to the applicability remain to be resolved and the most significant one is the blue device.¹⁰⁻¹¹ In the recent decades, development in blue electroluminescent materials have made a great progress,¹² especially in terms of both the color purity and the device efficiency.¹³ One of the most typical and the earliest organic electroluminescence phenomena was discovered in the single-crystal anthracene by Pope and coworkers in 1963.14 However, it is easy to crystallize rather than to form the amorphous film. Therefore, pure anthracene is not suitable for OLED devices. Thereupon, materials chemists modified anthracene to synthesize multiform anthracene compounds to improve its photoelectric properties.¹⁵⁻¹⁹ For the display applications, blue emission plays a crucial role in organic electroluminescence (EL), it not only acts as a part of Red-Green-Blue primary colors but also can integrate low-energyphosphorescence emitters to compose the hybrid white organic lighting-emitting devices (WOLEDs).²⁰⁻²² Recently, plenty of work has been done using phenanthroimidazole (PI) unit which demonstrates that PI group is conducive to be chosen as the central mojety of deep-blue emitters.²³⁻²⁴ When N1 and C2 positions of PI were modified with a benzene ring, one of the most common and typical derivatives 1.2-diphenvlphenanthroimidazole (PPI) (Scheme 1) was obtained.²⁵⁻²⁶ The PPI group is a nitrogen-containing heterocyclic conjugate group with a rigid plane conjugated structure possessing excellent properties such as high fluorescence quantum yield and wide light absorption, which makes it very attractive to be employed as a building block for the preparation of blue-emitters.²⁷⁻³⁰ PPI can effectively reduce the energy loss of non-radiation transition and exhibits good thermal stability.³¹ Two distinct nitrogen atoms in the imidazole ring render PPI to have a bipolar in nature, which indicates that PPI can not only be used as an electron acceptor when combined with a strong electron donor group but also has the ability of donating electron when coupled with an electrondeficient group or a weak electron donor group.³²⁻³⁴

Owing to their good hole transport properties performance and high energy band-gap, aromatic amines are widely used in the design of OLED materials. Among them, triphenylamine (TPA) (Scheme 1)³⁵⁻³⁶ and carbazole are the most representative integrants. Carbazole shows good optical and electronic properties, and possesses high triplet energy level inducing there is a small energy gap between triplet state and singlet state which is beneficial for intersystem crossing (ISC).³⁷ The lone pair of electrons present on the N-atom of carbazole makes it to be a good electron donor. However, after modified with a phenyl, for example, 9-phenyl-carbazole (PCz), the ability as an electron

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donor will be weakened.



Scheme 1. The chemical structures of PPI (a₁), TPA(a₂), PCz (a₃) and modifying PPI with TPA (triad-1), PCz (triad-2), phenyl group of PCz (triad-3) respectively at the site of C3 and with phenyl group of PCz (triad-4) and PCz at the site of C3'(triad-5).

Previously, a lot of fluorescent molecules based on PPI, TPA and PCz were developed as the emitters for OLED devices, and most of the work has been focused on the redox potential, the highest quantum efficiency $(\mathsf{EQE})^{38}$ and other electroluminescence performances of the OLED device. However, the excited state transitions and its dynamics were scarcely deeply understood for the photo-functional molecules consisting of PPI, TPA and PCz moieties. Here, a PPI couples with two TPA or PCz moieties forming two kinds of asymmetrical ternary structures, which are designed and synthesized to explore the nature of charge transfer (CT) in a series of innovative asymmetrical tripartite PPI-TPA/PCz triads (Scheme 1). Ultrafast time-resolved transient absorption spectroscopy has become a powerful technique to explore a range of excited states and CT dynamics of molecules.³⁹⁻⁴¹ By the combination of femtosecond/nanosecond transient absorption (fs-TA/ns-TA) spectroscopies and excited state theoretical calculations, the completely photophysical and photochemical arches of PPI-TPA/PCz triads were depicted.

Results and Discussion

Absorption and emission studies on the fragments and triads. Figure 1a shows the ground-state absorption spectra of the molecular fragments like PPI, TPA and PCz dissolved in DMF with the same concentration. PCz showed the maximum absorption band at 280 nm and the shoulder absorption peaks at 325 nm and 340 nm. In contrast, TPA showed a broad absorption peak centered at 300 nm. PPI has the absorption peaks at 312 nm and 340 nm which are overlapping with that of TPA and PCz, beyond that while PPI has an extra absorption peak at 360 nm. Under the same concentration, the absorption intensity of PPI above 320 nm are higher than that of PCz and TPA, PPI's molar absorption coefficient (ϵ_1 =2.23×10⁴ L·mol⁻¹·cm⁻¹) is higher than that of PCz $(\epsilon_2=1.44\times10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$ and TPA $(\epsilon_3=5.26\times10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$. The preparation methods of PPI-TPA/PCz molecular triads by systematical synthesis methods are given in the Supporting Information (Figure S1-S4), their absorption spectra are changed a lot (Figure 1b). All the absorption bands are broadened, the absorption peak's edge of PPI-PCz triads is close to 400 nm. In contrast, the absorption band's edge of triad-1 has reached 425

nm. Moreover, the main broad absorption bands of TPA for triad-1 have been observed to red-shift from 300 nm to 360 nm. These changes are attributed to the extensive conjugated system after the construction of the tripartite structure instead of CT in the ground state. The detail information will be discussed in the fs-TA part.

Figure 1c shows the photoluminescence (PL) spectra of PPI, PCz and TPA. PCz and TPA exhibit an ultraviolet emission peak at 365 nm after the irradiation of 300 nm whereas the emission peak of PPI lies at 390 nm. However, when they are combined into the asymmetrical tripartite triads' structures, the emission peaks have red-shifted to the deep blue region (Figure 1d). The maximum fluorescence emission peak of PPI-PCz triads lies at 420 nm which is red-shifted for 55 nm compared with that of PCz and for 30 nm compared with that of PPI, respectively. The triad-1's (PPI-TPA) emission peak locates at 466 nm which is redshifted for nearly 100 nm compared with that of TPA and for 76 nm compared with that of PPI. The fluorescence intensity of TPA is weaker than that of PPI and PCz by an order of magnitude in the same concentration, but the fluorescence intensity of triad-1 is excellent and its fluorescence quantum vield is close to 100%. which is same as that of the triads of PPI-PCz (Table S1). This reveals that when these asymmetrical tripartite triads structures are constructed successfully, their excited states' evolution channels have wide differences with the photo-behavior of the individual PCz, TPA and PPI. Therefore, it is worth to uncovering the intrinsic mechanism and the various effects which induce those differences between the triads and individual moieties.



Figure 1. (a) The OV-VIS absorption spectra of PC2, TPA and PPI absorved in DMF with the same concentration of 5 mM. (b) Shown are the normalized absorption spectra of the triads **1-5** dissolved in DMF. (c) The normalized emission spectra of PCz, TPA and PPI dissolved in DMF with the same concentration of 5 mM, the excitation wavelength is 300 nm. (d) The normalized emission spectra of the triads **1-5** dissolved in DMF, the excitation wavelength is 330 nm.

Femtosecond transient absorption studies on the evolution channels of triads.

Fs-TA spectroscopy can detect and trace the excited states and transient species after the excitation of the molecules in a specific timescale.⁴²⁻⁴³ The studies of PPI-TPA/PCz triads are measured in a strong polar organic solvent such as N, N-Dimethylformamide (DMF) and a non-polar organic solvent such as Dichloromethane (DCM), polar and non-polar solvent may aid to probe the solvent polarity's influence on the dipole-moment of excited states and the rate of charge separation (CS) state.^{44,45} Fs-TA experiments were performed to monitor the excited states

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Figure 2. The fs-TA spectra of triad-1 recorded in a DMF solution after 330 nm excitation. (a) The 3D fs-TA image of triad-1. The process of triad-1 (b) 0.19 ps to 1.78 ps, (c) 1.78 ps to 21.7 ps, (d) 21.7 ps to 118 ps, (e) 118 ps to 6.53 ns. (f) the global fitting dynamics (top) and the EADS (bottom) of triad-1.

evolution of the triad-1 in DMF solution under the excitation of 330 nm (Figure 2). Figure 2a indicates that a vivid 3D image can be obtained, the fs-TA spectra shows that the triad-1's main excitedstate absorption (ESA) peak locates at 623 nm, the ground state bleaching (GSB) locates at 360nm and stimulated emission (SE) band appears at 466 nm. Figure 2b-e displays four distinct processes after the photoexcitation. Firstly, two positive peaks centered at 520 nm and 621 nm are increased immediately, which are attributed to the popularity of the excited states from a ground state (S₀) to a higher excited state (S_n ($n \ge 1$)) under 330 nm excitation in a sub-picosecond time scale from 0.19 ps to 1.78 ps. After that, the transient spectra have changed significantly, the transient absorption spectra are a red-shift from 400 nm to 411 nm and the SE move from 435 nm to 467 nm (Figure 2c), which is associated by the electron transfer from the donor to the acceptor. The observation of the apparent isosbestic points at 462 nm and 575 nm indicates that the complete conversion from the singlet excited state to the CS state among triad-1 from 1.78 ps to 21.7 ps. After reaching the maximum extent of ICT, the transient absorption peaks do not show any change in the intensity as well as wavelength shift along the train of delay time from 21.7 ps to 118 ps (Figure 2d). This is probably due to the strong stability of the excited CS state of triad-1, which indicates that DMF solvent has little effect on its dipole moment. Ultimately, the appearance of the isosbestic points at 400 nm, 420 nm and 515 nm suggests the excited CS state of triad-1 solely return to the ground state by the charge recombination, which causes the GSB at 364 nm and SE at 467 nm, and positive peaks at 415 nm and 621 nm to drop out to zero gradually (Figure 2e). To clearly describe the photophysical processes of the compounds upon photoexcitation, the evolution associated difference spectra (EADS) of triad-1 (Figure 2f, bottom) were obtained by the global fitting, these results were outputted from Glotaran (a GUI software

for the "R" package, "TIMP")⁵¹. Figure 2f (top) presents each evolution associated spectra (EAS) in the EADS corresponding to the lifetime values which were obtained by the global fitting.

To further explore the nature of ICT process, a non-polar solvent DCM was used in the fs-TA experiments, the similar excited state evolution channels of triad-1 were observed in DCM solvent (Figure S5). But the maximum wavelength of transient absorption peak is drifted, the SE peak has a blue-shift from 467 nm in DMF to 452 nm in DCM. This also demonstrates that the second process is the ICT because the polar solvent leads to the transient absorption of ICT having a red-shift comparing to the results of non-polar solvent of triad-1.

Like the fs-TA results of triad-1 obtained in a DMF solution, the results of PPI-PCz triads are shown in Figure 3. It is obvious that the transient absorption peaks of triad-2, triad-3, triad-4, and triad-5 lie at 600 nm, 589 nm, 569 nm, and 640 nm, whereas their SE peaks take the positions at 425 nm, 434 nm, 430 nm and 433 nm, respectively. The detailed excited states evolutions of these triads are presented in Figure S6-S9. The phenomena of triad-2, triad-3, triad-4, and triad-5 are analogous to that of triad-1, in the same way, there are four processes including the generation of the excited states, ICT, CS state and charge recombination which are obviously represented in their EADS. In Figure S6 and S10, the isosbestic point of the triad-2 blueshifts from 467 nm in DMF to 450 nm in DCM solvent, which is caused by the energy level of CS state being higher than that of polar solvent. Other triads also exhibit different degrees of blue-shift in DCM solvent. Compared with the results of these samples dissolved in the non-polar organic DCM solvent (Figure S10-S13), all the SE peaks show little blue- shift in contrast to the strong polar solvent DMF. In a word, the results of fs-TA reveal that the solvent polarity will evidently affect the property of CS state of the five PPI triads.

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Figure 3. The 3D images of fs-TA for the PPI triads in DMF solution (a) triad-2, (b) triad-3, (c) triad-4 and (d) triad-5.

To trace the evolution of excited states and transient states of fs-TA spectra for all the triads, the global fitting was used to fit the dynamics of fs-TA spectra for all the triads, the lifetimes of various processes are listed in Table 1. When we testify the global fitting, four exponential function was found to gain the better dynamics fitting for the fs-TA data. This reveals that there are four excited state decay processes after the excitation for the triads, which is consistent with the four processes being observed in Figure 2 and Figure S5-S13. For all the triads, the first process is attributed to the formation of their excited state, their lifetimes are within 1ps; the second τ_2 lifetime is accounted by the ICT as well as emitting fluorescence for the triads; the third time period of τ_3 is associated by the CS state, in this case, the rearrangement with the surrounding solvent may stabilize the dipole moment of the excited CS states. And then finally, SE peak gradually disappears, so the fourth τ_4 lifetime is assigned to the charge recombination for all the triads.

Table 1. Summary of the dynamics for all the triads measured by fs-TA in DMF / DCM solvent, respectively, pumped by 330 nm

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	triads	$\tau_1 \ /ps$	τ_2/ps	τ 3 /ps	τ_4/ps
	1	0.53/0.46	4.65/2.37	653/396	1723/1898
	2	0.62/0.53	12.75/6.90	622/271	1667/1481
	3	0.71/0.54	9.93/3.51	597/465	1797/1910
	4	0.61/0.54	14.90/7.38	552/224	2052/1485
	5	0.64/0.50	17.90/9.30	866/385	2416/1732

Compared to the dynamics processes obtained in DCM solvent for all the triads, the data obtained in DMF solvent displays distinct features compared with that recorded in DCM solvent for the triads. The lifetimes of ICT (τ_2) and solvent rearrangement (τ_3) in DMF solvent are much longer than that of in DCM solvent. This reveals that the polar solvent makes the ICT to be more stable, which costs more time to produce a steady CS state. In addition, Table 1 also shows that the triad-5 spends the longest lifetime for ICT, and the triad-1 costs the minimal lifetime no matter what kind of solvent it dissolves. This indicates that the electronic nature of moieties, asymmetrical tripartite structure (combined positioned of PCz) also has great contribution effects on the ICT process. The above discussion confirms that these triads would transfer the electron in the excited state rather than in the ground state, the solvent polar, molecular structure and combined position of PCz would affect the rate of ICT. It must be noted that PPI is a bipolar molecule, PPI has two possible roles (donor or acceptor) in the triads. Therefore, the next step will verify the direction of the ICT process.

Direction of electron transfer between PPI and TPA/PCz triads.

Traditionally, carbazole is a kind of strong electron-donating group because of the lone pair electrons in the N atom. However, after substituting a benzene ring on the N atom, the lone pair electrons will be delocalized to the benzene ring, which will visibly diminish the ability of giving electrons of carbazole. When a novel molecular structure was designed by the constitution between PCz and bipolar PPI, the direction of ICT in the triads is vague to be identified. Therefore, this part focuses on the ICT direction in the PPI-PCz triads. Figure 1a suggests that 360 nm pump light can excite the PPI individually. Fs-TA experiments pump by 360 nm were also performed for all the triads, the excited states evolution of fs-TA pump by 360 nm are almost same as the results under the irradiation of 330 nm whether the spectrum (Figure S14-S17) or the lifetime (Table S1). Under the 330 nm and 360 nm pump excitation, all the triads are expected to transfer the electron from PPI to PCz. To further verify this speculation, ns-TA experiments were carried out to monitor the excited states and transient states of molecular fragments PPI and PCz.

Figure 4a displays the ns-TA results of PPI in a deoxygenated DMF solvent. The major ESA peak locates at 473nm which is distinct from the results of fs-TA for all the PPI triads. The kinetic fitting at 473 nm shows that PPI has a short lifetime of τ_1 =7.6 ns and a long lifetime of τ_2 =16.5 µs (Figure 4d). In order to confirm that the long life-time transient state is a triple state of PPI, the oxygen was purged into the solution. The long lifetime transient state was quenched by the oxygen and the lifetime dropped down to 0.16 µs (Figure S18). This demonstrates that the long lifetime transient state of PPI has a triplet state nature. Therefore, ns-TA quenched experiments for PPI demonstrates that PPI will undergo the ISC to produce the triple state after the excitation by 330 nm. Given that the longest lifetime τ_4 of PPI triads is around 1.5 ns for the results of fs-TA discussed previously, which is unprecedentedly shorter than the long lifetime of ns-TA for PPI. This demonstrates that PPI intends to transfer the electron to the acceptor in the triads rather than undergoes the ISC to generate the triple state in the triads. In Figure 4b, the 3D image of ns-TA results for PCz in a deoxygenated DMF solvent show that the major ESA peak locates at 408 nm which is also different to the results of fs-TA of PPI triads. The kinetic fitting at 408 nm gains the lifetimes including τ_1 =15 ns and τ_2 =2.47 µs (Figure 4e), which is also longer than the lifetime τ_4 of PPI triads, but the 2.47 μs is much shorter compared to the long lifetime of PPI 16.5 µs. To figure out the direction of electron transfer, the ns-TA experiments were also carried out on the mixing solution of PPI and PCz. The results show that a main ESA peak can be observed at 470 nm which is characteristic feature peak of triplet state of PPI (Figure 4c).46 The ESA at 470 nm was quenched with the increase of the concentration of PCz. Figure 4f displays that the lifetime of triplet state of PPI gradually decreases (Figure 4f) while the lifetimes of 408 nm are getting longer and longer when the concentration of

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Figure 4. The 3D images of ns-TA spectra of PPI (a) and PCz (b) with a concentration of 5 mM in deoxygenated DMF. (c) The 3D image of ns-TA spectra of the mixed solution of PPI and PCz with the same concentration in DMF solution. The kinetic at 473 nm of PPI (d), at 408 nm of PCz (e) and at 473 nm of 5 mM PPI with the increase of the concentration of PCz (f) in deoxygenated DMF.

PCz increases (Table S2).

To further confirm the ICT, we have calculated the ESA of the cation or the anion of the molecular fragments like PPI, TPA and PCz. The calculated results shown that the oscillator strength value for the cation of PPI at 630 nm is 0.1838 and the oscillator strength value for the anion of PPI at 662 nm is 0.1478 nm. Therefore, the ESA peak of both the cation and the anion of PPI located at 650 nm (Figure S19). After the ICT, the transient absorption spectra at 623 nm (triad 1), 600 nm (triad 2), 589 nm (triad 3), 569 nm (triad 4), and 640 nm (triad 5) gradually increase (Figure 2a and Figure 3), this reveals that these transient absorption peaks are associated by the generation of the anion of PPI for triad 1 or the cation of PPI for triad 2-5 . In addition, we also calculated the ESA of the cation of TPA (TPA⁺) and the anion of PCz (PCz-), the results found that they have an overlapping peak at around 550 nm (Figure 19S). For triad 1, the transient absorption peak at 520 nm gradual redshift to 550 nm in Figure 2c indicates the produce of the TPA+. In addition, the transient absorption at 560 nm of the mixing solution of PPI and PCz is obviously higher than the individual PPI and PCz at 2 µs under the same concentration (Figure 19S(f)), which suggests the generation of the PCz-in the mixing solution after ICT. Therefore, these evidences support that the electron will be transported from PPI to PCz in the triads under the irradiation of 330 nm light.

TD-DFT calculations for electronic and hole density of excited states of triads.

Figure 5 shows the electronic and hole density patterns, isosurface of C_{ele} and C_{hole} , Δr index, oscillator strengths, and the energy level of the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) of singlet excited states for triad-1 and triad-2. The results convey that triad-1 will be excited to the first singlet excited state (S₁) with a high probability for a larger oscillator strength (f=0.823) while the value of oscillator strength of the second singlet excited state (S₂) is very small. In contrast, the oscillator strength of the S₂ in triad-2 has a greater number (f=0.75), however, the value of oscillator strength of the S1 is less, which means that triad-2 will reach the S2 state for a great proportion after irradiation. The results of other triads are displayed in the SI (Figure S20-S22). The calculated results reveal that all the triads composed by PPI and PCz have a higher probability to be excited to S2. As shown in Figure 5, when triad-1 is excited to S₁, the electron cloud density of the HOMO orbital mainly locates in TPA part while the electron cloud density of the LUMO orbital mainly locates in PPI part and benzene part. When triad-2 is excited to S2, the electron cloud density of the HOMO orbital mainly locates in PPI part while the electron cloud density of the LUMO orbital mainly locates in PCz part and benzene part. Moreover, other PPI-PCz triads also have the same tendency as triad-2 (Figure S20-S22). Above results prove that PPI part plays two different roles between triad-1 and PPI-PCz triads. PPI acts as the acceptor when connected with TPA in triad-1 while it becomes as the donor part when constructed with PCz moiety in the triad-2 to triad-5.

Furthermore, the distribution of hole and electron in the triads is necessary to expound the extent of ICT. The hole and electron can be defined in different ways. Lu and co-workers⁴⁷ gave a new definition that the distribution of the hole signifies where the electron leaves, and the distribution of the electron is where the excited electron stays in the excited state. In the iso-surface of hole & electron, the green part is the positive side, corresponding to the increase in the electron density of the excited state relative to the ground state, and blue part is the opposite side. According to this rule, the electrons are more concentrated on the PPI side while the TPA side is occupied by holes in the S₁ state for triad-1. However, the completely different phenomena are observed in PPI-PCz triads because the PPI part plays an electron acceptor role in triad-1 but an electron donor role in PPI-PCz triads. The above results are consistent with the calculated distribution of electron cloud density on HOMO and LUMO orbitals. The isosurface of hole & electron can be visualized as two ellipses named

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Figure 5. The calculated data of the electronic and hole density patterns, iso-surface of Cele and Chole functions, Δr index, oscillator strengths, and energy level and electron density of HOMO and LUMO orbital of the singlet excited states for triad-1 and triad-2.

Chole & Cele, while the distance between the center of the blue and green ellipses (corresponding to the centroid position of the hole and the electron) is the Δr index. Table 2 shows the Δr index and oscillator strengths. The Δr of triad-1 in the S₁ state is 3.15 Å, obviously, this distance can be considered as CT excitation.⁴⁸ All the PPI-PCz triads have a larger value of oscillator strengths in S₂ state, this reveals that these triads will be probably excited to S₂. Interestingly, given that the possibility of observing anti-Kasha phenomenon in other fundamental reactions, the excited-state intramolecular proton-transfer reaction once demonstrated anti-Kasha behavior.⁴⁹ The anti-Kasha reaction rate depends on the interplay with vibrational relaxation, internal conversion and radiative or nonradiative relaxation to the ground state. In this work, the ICT process of PPI-PCz triads may take place in S₂ state,

it may call as anti-Kasha's ICT. The Δr values of S_2 state of triad-4 and triad-5 are maximum, in contrast, the Δr of S_2 state of triad-3 is minimum. Figure 6 shows that the calculated Δr values of S_2 state for PPI-PCz triads are related with the lifetime of ICT process (τ_2) observed by the fs-TA experiments. Therefore, the Δr index may also determine the lifetime of ICT in the triads.



Figure 6. The correlation between Δr and τ_2 lifetime in the triads 2-5.

Conclusion

The present study has explored the properties of excited states and interchromophoric interactions of two kinds of tripartite PPIbased bipolarity triads 1-5 by UV-vis absorption, fluorescence, fs-TA/ns-TA and DFT calculations. The ICT does not occur in the

index and oscillator strengths (f) in the singlet	Figure 6 The correl

Table 2. The summary of the Δr index and oscillator strengths (f) in the single	t
excited states of PPI triads 1-5.	

	S1		S ₂		
	f	$\Delta \mathbf{r}$	f	$\Delta \mathbf{r}$	
triad-1	0.823	3.15 Å	0.325	4.64 Å	
triad-2	0.48	3.40 Å	0.75	2.63 Å	
triad-3	0.14	4.84 Å	0.84	1.02 Å	
triad-4	0.086	5.20 Å	0.73	3.23 Å	
triad-5	0.12	6.0 Å	1.12	3.21 Å	

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ground-state which is proved by no new redshift UV-vis absorption peak and fluorescence peak detected in DMF solvent. All the triads showed almost 100% absolute PL quantum yield at blue range. Excited states studies determined that the ICT is crucial process to account for the enhancement of the fluorescence for all the triads. Fs-TA results show that there are four processes (Scheme 2) including the popularity of the excited states, ICT, CS state and charge recombination. Ns-TA studies demonstrate that PPI is electron acceptor moiety in triad-1 when connecting with TPA chromophore while PPI is electron donor part in the triads 2-5 when building up with PCz chromophore. The electronic nature of moieties, asymmetrical tripartite structure, the polarity of solvent, excited ICT states and CS distance Δr index will affect the direction of electron and lifetime of ICT of all the triads. Interestingly, the solvent polarity does not change the dipole moment and energy of the CS state because the transient absorption of CS state is remained constant during the third process (τ_3) . Eventually, the calculated results demonstrate that PPI-PCz triads demonstrate an anti-Kasha's ICT process and the calculated Δr between C_{ele} and C_{hole} can match very well with the lifetime of the ICT process (τ_2) observed by fs-TA experiments. This study is crucial for the design and application of these luminescent materials for OLED devices in future.



Scheme 2. The visualization of the whole excited state evolution channels in the triads.

Experimental Section

Experimental and Computational Methods

Sample preparation.

Synthesis: A 100 mL, flame dried, two-necked round-bottomed flask was equipped with a 2.4 cm Teflon-coated magnetic oval stir bar. The side-neck was fitted with a rubber septum using an inlet needle connected to a Schlenk line. The central neck was equipped with a water-jacked reflux condenser. The assembled apparatus is charged with 2Br-PPI (1eq, 2mmol), Boric acid derivatives (2.5eq, 5mmol), saturated potassium carbonate solution (10ml), EtOH (10ml), Toluene (25ml) with argon bubbling 45 mins. After that, Pd (PPh3)4 (5% equal, 0.1mmol) was added into the solution. The reaction was processed in 90 °C with TLC plate monitoring. After being cooled to room temperature, the solution was washed with 40 mL water three times and extracted with dichloromethane; then, collected organic solution was dried with anhydrous Mg₂SO₄ and concentrated by rotary evaporation. Finally, the residue was purified by column chromatography (petroleum ether: $CH_2Cl_2 = 2$: 1) to obtain the pure white powder.

Synthesis of 4-biTPA-PPI: Yield: 1.5 g (82%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.81 (d, *J* = 8.5 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.76 (dt, *J* = 25.0, 8.6 Hz, 4H), 7.59 (ddd, *J* = 34.7, 23.4, 8.7 Hz, 10H), 7.43 – 7.23 (m, 11H), 7.23 – 7.02 (m, 15H).

Synthesis of 4-biPCz-PPI: Yield: 1.8 g (88%) ¹H NMR (400 MHz, CD₂Cl₂) δ 8.73 (d, J = 8.3 Hz, 1H), 8.68 (d, J = 8.3 Hz, 1H), 8.51 (d, J = 1.6 Hz, 1H), 8.33 (d, J = 1.5 Hz, 1H), 8.17 (d, J = 7.7 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.82 – 7.15 (m, 31H).

Synthesis of 4-bi(N-PCz)-PPI: Yield: 1.5 g (83%) ¹H NMR (400 MHz, CD₂Cl₂) δ 8.84 (d, *J* = 8.4 Hz, 1H), 8.78 (d, *J* = 8.3 Hz, 1H), 8.21-8.13 (m, 4H), 8.08-8.02 (m, 4H), 7.91-7.65 (m, 15H), 7.62-7.26 (m, 16H).

Synthesis of 3-bi(N-PCz)-PPI: Yield: 1.4 g (82%) ¹H NMR (400 MHz, CD₂Cl₂) δ 8.84 (d, *J* = 8.4 Hz, 1H), 8.78 (d, *J* = 8.3 Hz, 1H), 8.20 (t, *J* = 8.0 Hz, 4H), 7.59 (dddd, *J* = 30.6, 24.2, 20.2, 16.0, 4.8 Hz, 33H).

Synthesis of 3-biPCz-PPI: Yield: 1.4 g (82%) ¹H NMR (400 MHz, CD₂Cl₂) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.17 – 8.03 (m, 3H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.77 – 7.14 (m, 33H).

A. Femtosecond transient absorption (fs-TA) experiments: The fs-TA measurements were performed with an apparatus and methods detailed previously and details are given in references 42 and 43. Very briefly, fs-TA spectra were obtained by employing the harmonic (330 and 360 nm light) for the pump pulse and white-light continuum (350–800 nm light) for the probe pulse generated from the 800 nm output of a femtosecond regenerative amplified Ti:sapphire laser system For the measurements here, a solution of 40 mL was passed through a 2 mm thick cell, excited by a 330 and 360 nm pump pulse and then interrogated by the white light continuum pulse.

B. Excited state calculations: To have a better understanding about the direction of CT for all the triads and to quantify the extent of ICT, density function theory (DFT) and time-dependent density function theory (TD-DFT) calculations were used to optimize molecular structure and study their excited states. The calculations were conducted by employing B3LYP method and 6-311G** through the Gaussian 16 program package.⁵⁰ After that, the Multiwfn program⁴⁷ was used to analyze and visualize hole-electron distribution, transition density and calculate Δr index to measure CT length.

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Two types of asymmetrical tripartite triads (PPI-TPA and PPI-PCz) have been designed for deep-blue luminescent materials with a high fluorescence quantum yield of nearly 100%. For these novel triads, the electronic nature of moieties, asymmetrical tripartite structure and the distance of electron-hole of these triads as well as the polarity of solvent determine the lifetimes of excited state intramolecular charge transfer (ICT). Interestingly, the charge transfer direction among the triads is adjustable.