Singlet Energy Transfer and Photoinduced Electron Transfer in Star-Shaped Naphthalimide Derivatives Based on Triphenylamine

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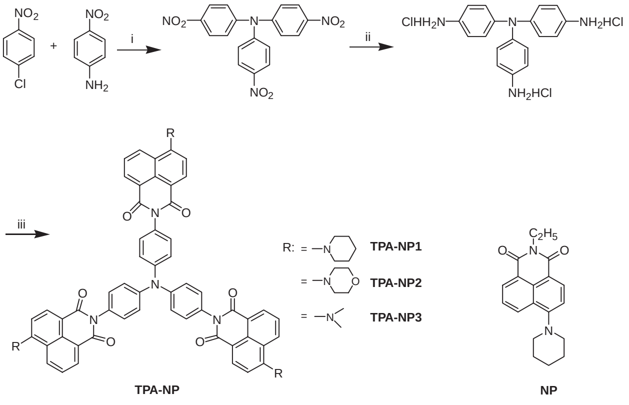
A series of star-shaped naphthalimide derivatives (TPA-NP) were synthesized with a triphenylamine (TPA) core and chromophores at the rim. Their steady-state absorption, fluorescence, and transient fluorescence spectra were investigated, indicative of severely fluorescent quenching with regard to the corresponding 1,8-naphthalimide (NP) parent chromophores. Excitation into either the triphenylamine or naphthalimide absorption bands results in the occurrence of singlet energy transfer and photoinduced electron transfer (PIET) effectively. Single photon-counting experiments show a fast charge separation and a thermally activated back reaction. As a consequence, the fluorescent lifetime of the naphthalimide moiety in the system of TPA-NP is reduced by more than an order of magnitude, which mainly arises from the intramolecular PIET process of TPA and naphthalimide. The kinetics and PIET mechanism involving TPA-NP were elucidated.

Recently, two concepts toward amorphousness and bipolarity have received growing attention for the design of organic electroluminescent (EL) materials. Amorphous materials[1] can form stable glasses with high glass transition temperatures (T_g), which possess excellent processability, transparency, isotropic properties, and most important the absence of grain boundaries. Amorphous thin films with high T_g in OLEDs are less vulnerable to Joule heating, which accelerates the formation of crystalline boundaries. Also, EL materials for use in the emitting layer should desirably possess a bipolar character,[2] i.e., both electron-donating and electron-withdrawing properties, to permit the formation of both stable cation and anion radicals. Of particular interest are emitting materials that can form homogeneous thin films with morphological and thermal stability, thus meeting the energy-level matching for charge–carrier injection and acceptance of both holes and electrons.[3]

However, the intra-molecular photo-induced electron transfer (PIET) on the luminescence efficiency in bipolar emitters and various donor–acceptor covalently linked systems has not drawn much attention.[4,5] Electron transfer (ET) is the most elementary and ubiquitous of all chemical reactions, and plays a crucial role in many essential photophysic processes.[6] PIET can take place from polymers with electron-donor abilities, such as polysilane, polygermane, poly(vinylcarbazole), and polythiophene, to the triplet states of fullerenes in polar solvents.[7] Such electron transfer from their lowest excited singlet or triplet states always reduces the electron acceptor, and even produces charge separation, thus resulting in severe quenching in luminance.[8] An enhanced understanding of the PIET effect on the multi-component luminescent properties is significant for developing novel highly efficient chromophores. Considering the high electron-donating and low oxidation potential properties of triphenylamine, PIET in the luminescent materials containing triphenylamine unit might be very possible to take place in the solid state or solution.[9] To further explore these effects, here we consider the intra-molecular photo-induced energy- and electron-transfer behavior in star-shaped naphthalimide derivatives based on triphenylamine (TPA-NP shown in Scheme 1). Our results suggest that when incorporating a triphenylamine unit to the chromophore for designing bipolar or star-shaped emitters, the fluorescence quenching induced by possible through-bond PIET should be desirably considered. In contrast to the corresponding 1,8-naphthalimide parent chromophores, there exists severely fluorescent quenching in the system of TPA-NP due to effective singlet energy transfer and PIET. The fluorescent lifetime of the naphthalimide moiety in the system of TPA-NP was reduced by more than one order of magnitude. We also considered the PIET mecha-



Scheme 1. Synthetic routes of target compounds TPA-NP, and chemical structure of reference compound *N*-ethyl-4-piperidin-1-yl-1,8-naphthalimide (NP). Reaction conditions: i. DMF, K_2CO_3, Cu, reflux for 48 h; ii. $SnCl_2$/HCl (3:1), reflux for 5 h; iii. Corresponding naphthalic anhydride, 2-mehoxyethanol and piperidine, reflux for 16 h.

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nism involving TPA-NP by thermodynamic and transient fluorescent analysis. To the best of our knowledge, the model of TPA-NP is the first example, in which PIET occurred from the imide side of naphthalimide to the naphthalene ring.

Experimental

General. The melting points were measured on a X4 micromelting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer. Mass spectra were determined by VG12-250 mass spectroscopy. Absorption and fluorescence spectra were recorded on a Varian Cary 500 and a Varian Cary Eclipse, respectively. The fluorescence lifetimes were detected by an Edinburgh FL900 single-photon counting system.

Cyclic voltammetry (CV) were carried out on a CHI 800 electrochemical instrument with a platinum electrode using millimolar solutions in CH_2Cl_2 containing supporting electrolyte tetrabutylammonium perchloride (0.1 $mol\,L^{-1}$) in a cell with three electrodes and a potentiostat assembly. The potentials were measured at a scan rate of 0.1 V/s, a Ag/AgCl electrode was used as a reference electrode. Tri(4-amino)phenylamine hydrochloride was synthesized according to a previous reference.[10]

Synthesis of TPA-NP1. A mixture of tri(4-amino)phenylamine hydrochloride (175 mg, 0.44 mmol), 4-piperidin-1-yl-1,8-naphthalic anhydride (390 mg, 1.39 mmol), piperidine (1.0 mL), and 2-methoxyethanol (17 mL) was refluxed for 16 h under an argon atmosphere. After being cooled and filtrated, the filtrated cake was recrystallized from 2-methoxyethanol to give a bright yellow solid in 60% yield. mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.67 (m, 6H, CH_2), 1.85 (m, 12H, CH_2), 3.19 (s, 12H, CH_2), 7.14 (d, $J = 7.9$ Hz, 3H, naphthalene-H), 7.16 (d, $J = 8.6$ Hz, 6H, benzene-H), 7.37 (d, $J = 8.6$ Hz, 6H, benzene-H), 7.64 (t, $J = 7.9$ Hz, 3H, naphthalene-H), 8.39 (d, $J = 8.4$ Hz, 3H, naphthalene-H), 8.48 (d, $J = 8.1$ Hz, 3H, naphthalene-H), 8.55 (d, $J = 7.2$ Hz, 3H, naphthalene-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 24.36, 26.24, 54.55, 114.79, 116.05, 123.35, 124.79, 125.42, 126.38, 129.57, 130.33, 130.88, 131.41, 133.05, 147.19, 157.53, 164.34, 164.85. FAB-MS: m/z [M^+] 1082. Other two compounds were synthesized by a similar method.

TPA-NP2 was prepared from 4-morpholin-4-yl-1,8-naphthalic anhydride in 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.31 (m, 12H, CH_2), 4.04 (m, 12H, CH_2), 7.22 (d, $J = 8.2$ Hz, 3H, naphthalene-H), 7.26 (d, $J = 8.6$ Hz, 6H, benzene-H), 7.44 (d, $J = 8.6$ Hz, 6H, benzene-H), 7.75 (t, $J = 7.9$ Hz, 3H, naphthalene-H), 8.47 (d, $J = 8.4$ Hz, 3H, naphthalene-H), 8.58 (d, $J = 8.0$ Hz, 3H, naphthalene-H), 8.64 (d, $J = 7.2$ Hz, 3H, naphthalene-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 30.44, 53.45, 66.99, 115.06, 117.30, 123.55, 124.83, 125.94, 126.25, 129.57, 130.20, 130.27, 130.36, 131.59, 132.94, 147.24, 155.87, 164.21, 164.68. FAB-MS: m/z 1087 [M^+].

TPA-NP3 was prepared from 4-dimethylamino-1,8-naphthalic anhydride and tri(4-amino)phenylamine hydrochloride. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.14 (s, 18H, $-N(CH_3)_2$), 7.16 (d, $J = 8.2$ Hz, 3H, naphthalene-H), 7.23 (d, $J = 8.4$ Hz, 6H, benzene-H), 7.37 (d, $J = 8.5$ Hz, 6H, benzene-H), 7.70 (t, $J = 7.9$ Hz, 3H, naphthalene-H), 8.50 (d, $J = 8.5$ Hz, 3H, naphthalene-H), 8.54 (d, $J = 8.2$ Hz, 3H, naphthalene-H), 8.63 (d, $J = 7.2$ Hz, 3H, naphthalene-H). MS (ESI): m/z 983.1 [$M^+ + Na$].

Results and Discussion

Design and Synthesis of Star-Shaped Compounds TPA-NP. A series of star-shaped bipolar derivatives (TPA-NP shown in Scheme 1) were synthesized, which are based on the electron-donating triphenylamine (TPA) core and the electron-withdrawing naphthalimide (NP) chromophores at the rim. Naphthalimides due to their high fluorescence yield, good stability, and high electron affinity (about 3.1 eV) have been utilized as electron-transporting electroluminescent emitters.[11]

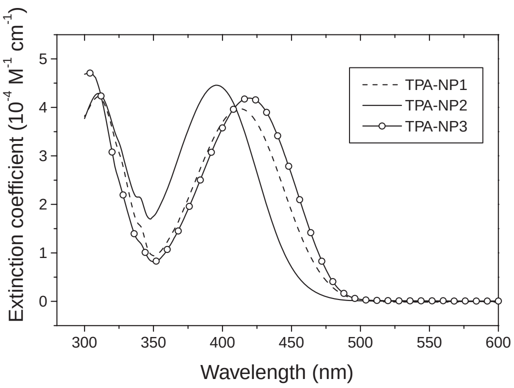

Fig. 1. UV–vis absorption spectra of TPA-NP in CH_2Cl_2.

Due to the extremely easy oxidation of the intermediate tri(4-aminophenyl)amine, we chose its hydrochloride to directly react with 4-substituted naphthalic anhydride in 2-methoxyethanol using excess secondary amine piperidine (Scheme 1). Here, piperidine plays double roles, i.e. as an imidization catalyst and an acid-trap for liberating HCl. We found that the imidization could achieve a satisfactory yield with the base catalysis of piperidine.[12] All molecular structures were confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectra.

Steady-State Absorption and Fluorescence Properties. Figure 1 shows UV–vis absorption spectra of star-shaped compounds, TPA-NP. A band peak at about 310 nm for these compounds is attributed to the absorption transition of the triphenylamine unit, while the absorption peaks characterized for the 1,8-naphthalimide moieties of TPA-NP1, TPA-NP2, and TPA-NP3 are located at 412, 396, and 420 nm, respectively (Table 1). The absorption peak variation of the naphthalimide moiety is due to a different substituent group effect at the 4-position of the 1,8-naphthalimide moiety.

Star-shaped compounds have an ideal architecture to study the interaction between the chromophores. To study this, we prepared a simple mixture solution of triphenylamine (TPA) and *N*-ethyl-4-piperidin-1-yl-1,8-naphthalimide (NP) as a reference (molar ratio = 1:3). As shown in the steady-state emission spectra of a simple mixture of TPA and NP (shown in Fig. 2), two obvious emission peaks at 361 and 515 nm correspond to emission of the triphenylamine and the naphthalimide units, respectively. The relative ratio of the integrated luminescence intensities of these solutions are listed in Table 1. If the fluorescence intensity of the NP unit for the reference system excited at 310 nm (TPA absorption maximum) is arbitrary defined as one unit, the relative fluorescence quantum yields of the 1,8-naphthalimide moiety under the same condition for TPA-NP1, TPA-NP2, and TPA-NP3 are 0.060, 0.018, and 0.117, respectively. Similarly, when directly excited at the corresponding absorption peak of the 1,8-naphthalimide moiety, TPA-NP1, TPA-NP2, and TPA-NP3 had relative fluorescence quantum yields of 0.052, 0.041, and 0.157, respec-

Table 1. Absorption and Fluorescence Data (1×10^{-6} mol L^{-1}), Oxidation Potentials and Calculated Energies of Electron Transfer for TPA-NP and Reference Compounds (TPA and NP) in CH_2Cl_2

Compds	$\lambda_{max}{}^{abs}$/nm ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1})	$\lambda_{max}{}^{flu}$/nm	$\eta_{TPA}{}^{a)}$	$\eta_{NP1}{}^{b)}$	$\eta_{NP2}{}^{c)}$	τ/ns	$E_{ox}{}^{d)}$ /V	HOMO /eV	ΔG_{et} /kcal mol^{-1}
TPA-NP1	310 (4.22) 412 (3.98)	518	0.337	0.060	0.052	0.095 (56.9%) 1.220 (43.1%)	1.19	5.47	−5.4
TPA-NP2	310 (4.29) 396 (4.46)	516	0.244	0.018	0.041	0.033 (59.1%) 2.800 (40.9%)	1.15	5.43	−4.5
TPA-NP3	304 (4.71) 420 (4.19)	508	0.302	0.117	0.157	0.112 (40%) 0.655 (60%)	1.08	5.36	−2.4
TPA	300 (7.20)	361	1.000				0.98		
NP		515		1.000	1.000	9.320 (100%)	1.12	5.50	

a) η_{TPA} is the relative fluorescence quantum yields of triphenylamine unit excited at 310 nm. The fluorescence intensity of reference compound TPA is arbitrary defined as one unit. b) η_{NP1} is the relative fluorescence quantum yields of 1,8-naphthalimide moiety excited at 310 nm. The fluorescence intensity of reference compound NP is arbitrary defined as one unit. c) η_{NP2} is the relative fluorescence quantum yields of 1,8-naphthalimide moiety excited at the absorption peak of 1,8-naphthalimide moiety. The fluorescence intensity of reference compound NP is arbitrary defined as one unit. d) The oxidation potential of reference ferrocene (Fc) vs reference electrode Ag/AgCl is 0.52 V.

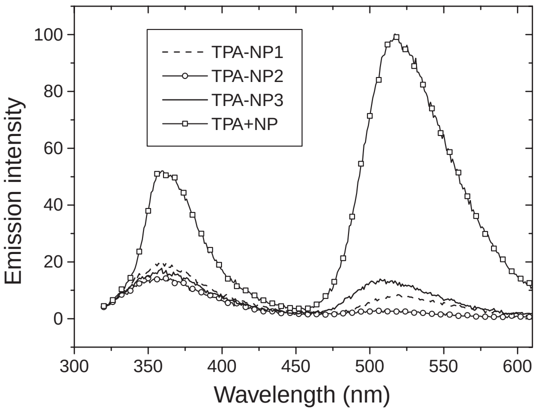

Fig. 2. Fluorescence spectra in CH_2Cl_2 excited at 310 nm: TPA-NP (1×10^{-6} mol L^{-1}), and the reference compound mixture of triphenylamine (TPA) and *N*-ethyl-4-piperidin-1-yl-1,8-naphthalimide (NP) (molar ratio = 1:3, TPA: 1.0×10^{-6} mol L^{-1}, NP: 3.0×10^{-6} mol L^{-1}).

tively. This demonstrates the existence of strong fluorescence quenching for the naphthalimide moiety bonded to a triphenylamine unit. Especially for TPA-NP1 and TPA-NP2, the emission intensities of the naphthalimide moiety are reduced by more than two orders of magnitude, and the quenching efficiency reaches as high as 95% in both cases of direct excitation (400 nm) and indirect excitation (310 nm).

Obviously, the intramolecular interaction between the two chromophores for TPA-NP is much stronger than the intermolecular interaction in the system of a simple mixture. This phenomenon is further supported by the fluorescence dependence on the solution concentration. The fluorescence from the simple mixture is much more significantly dependent on the concentration than that from TPA-NP. Indeed, when diluted for the simple mixture, almost no fluorescent quenching of these two chromophores is observed.

As can be seen in Fig. 3, there exists an overlap between the fluorescence of triphenylamine (peak at 361 nm) and the absorption of the 1,8-naphthalimide (peak at 410 nm). Thus, the singlet–singlet energy transfer (Förster-type energy transfer) from the triphenylamine unit to the 1,8-naphthalimide moiety occurred in the TPA-NP system.[13] It has an efficient spectral overlap and an energy transfer that results in significantly fluorescent quenching of the triphenylamine unit in TPA-NP. With respect to triphenylamine, the fluorescence intensities of the triphenylamine unit in the system of TPA-NP1, TPA-NP2, and TPA-NP3 are 0.337, 0.244, and 0.302, respectively (Fig. 2). However, an apparent paradox arises for the triphenylamine units in these star-shaped systems of TPA-NP, where such efficient singlet energy transfer from TPA to NP doesn't increase the fluorescence efficiency of the acceptor naphthalimide moiety. In other words, another nonradiative relaxation process might compete with the contribution from the singlet energy transfer, and then results in a quenching effect on the luminescence of naphthalimide unit. As a matter of fact, naphthalimide derivatives have been utilized as electron-transporting electroluminescent emitters with a high electron affinity (about 3.1 eV).[11] Therefore, the occurrence of PIET is very reasonable when incorporating some low oxidation potential units, such as triphenylamine, to the naphthalimide moiety.[9] The strongly fluorescent quenching of the naphthalimide moiety in the TPA-NP systems most likely results from the PIET between the triphenylamine (donor) and the naphthalimide

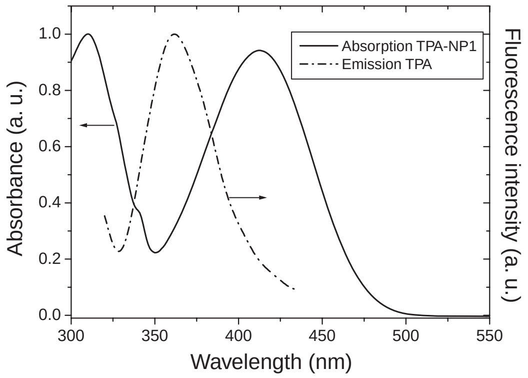

Fig. 3. Absorption spectra of TPA-NP1 in CH_2Cl_2 (1.0×10^{-5} mol L^{-1}), and fluorescence spectra of TPA excited at 310 nm in CH_2Cl_2 (1.0×10^{-5} mol L^{-1}).

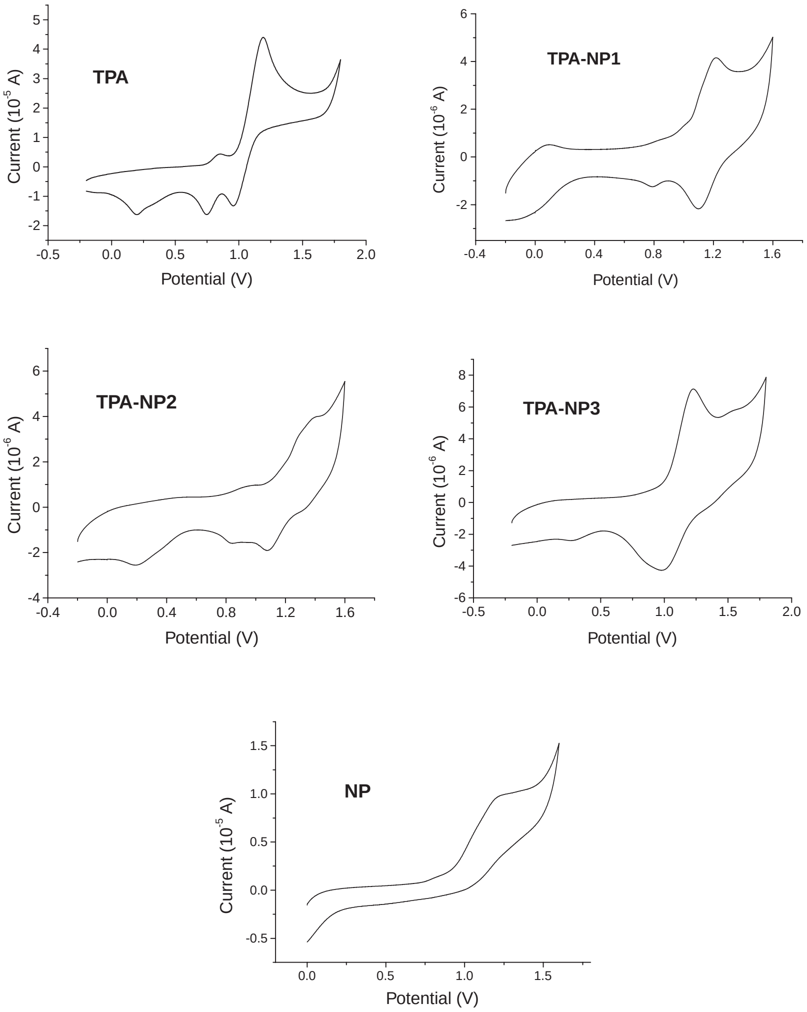

Fig. 4. Cyclic voltammograms of TPA, TPA-NP1, TPA-NP2, TPA-NP3, and NP in CH_2Cl_2.

units (acceptor), which is supported by the following electrochemistry and transient fluorescence study.

Electrochemical Properties and Thermodynamics. Cyclic voltammetry (CV) measurements were carried out in a conventional three-electrode cell using millimolar solutions in CH_2Cl_2 containing 0.1 $mol\,L^{-1}$ of the support electrolyte, tetrabutylammonium perchloride. Figure 4 shows cyclic voltammograms of TPA, TPA-NP1, TPA-NP2, and TPA-NP3 in CH_2Cl_2. The corresponding oxidation potentials are listed in Table 1. It should be noted that for TPA-NP compounds, the predominated oxidative sweep of triphenylamine peaks at 1.2 V, and is overlapped with an irreversible peak of the naphthalimide unit located between 1.10 and 1.30 V. The HOMO energy values for TPA-NP are also given in Table 1, which were calculated using a value of −4.8 eV for ferrocene (Fc) with respect to zero vacuum level. Also the optical edge of the absorption spectra was utilized to derive the band gap, and indirectly give the corresponding LUMO energy and reduction potential values.

In the TPA-NP system, PIET from the triphenylamine unit to the naphthalimide chromophore can be elucidated from the viewpoint of thermodynamics. The measured oxidation potentials and absorption spectral data show a quantitative estimation of the thermodynamic driving force (ΔG_{et}) for the PIET process. The ΔG_{et} values were calculated by the following Rehm–Weller equation:[14]

$$\Delta G_{\mathrm{et}} = 23.06[E(\mathrm{D}^+/\mathrm{D}) - E(\mathrm{A}^-/\mathrm{A}) - \Delta E_{0,0} - e_0{}^2/\alpha\varepsilon], \quad (1)$$

where $E(\mathrm{D}^+/\mathrm{D})$ is the donor oxidation potential (TPA unit), $E(\mathrm{A}^-/\mathrm{A})$ is the acceptor reduction potential (1,8-naphthalimide moiety), $\Delta E_{0,0}$ is the excitation energy of 1,8-naphthalimide moiety, and $e_0{}^2/\alpha\varepsilon$ is the energy gained in bringing the two radical ions; e_0 is the charge of an electron, ε is the static dielectric constant of solvent, and α is the distance between the donor and the acceptor. Molecular modeling shows that the distance between the donor and the acceptor is 4.76 Å. It was calculated that $e_0{}^2/\alpha\varepsilon$ is 0.024 eV in CH_2Cl_2; the resulting free energy values (ΔG_{et}) are listed in Table 1. These data show that electron transfer from TPA to NP is strongly favored.

Transient Fluorescence Spectroscopy and Electron Transfer. To further explore the nature of intramolecular luminescence quenching, the transient fluorescence of these compounds was investigated (the data listed in Table 1). The fluorescence decay of the naphthalimide moiety in the TPA-NP system has two contribution components with different lifetimes. As a case illustrated in Fig. 5, the fluorescence kinetics of TPA-NP1 can be fit to a dual-exponential decay with

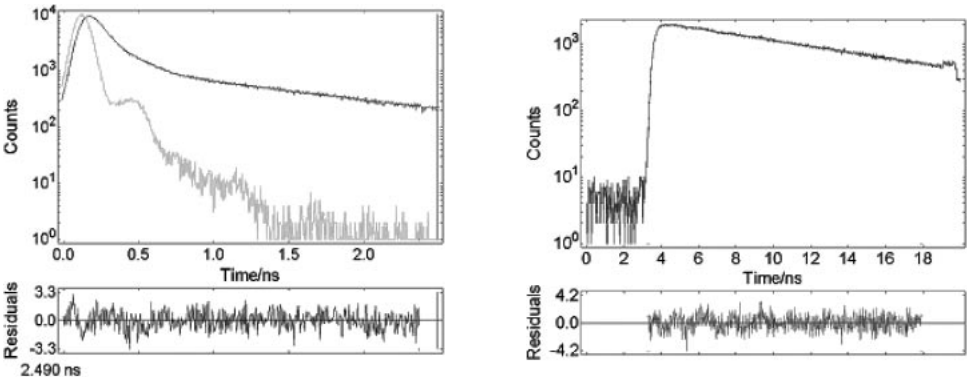

Fig. 5. Fluorescence decay profiles of naphthalimide moiety for TPA-NP1 (Left) and reference compound NP (Right) in CH_2Cl_2 (1.0×10^{-5} mol L^{-1}, $\lambda_{ex} = 410$ nm, $\lambda_{em} = 513$ nm).

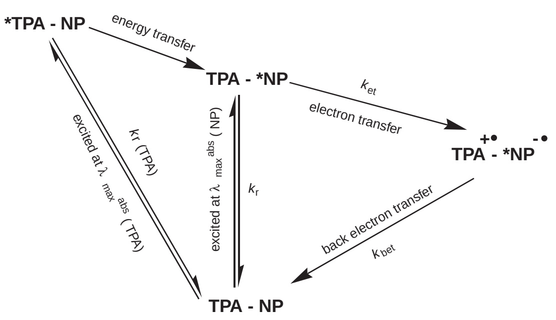

Fig. 6. Schematic diagram for energy transfer and electron transfer in TPA-NP.

lifetimes of 95 ps (56.9%) and 1.220 ns (43.1%). In contrast, the reference compound NP exhibits a single-exponential decay with a lifetime of 9.320 ns (100%). In the system of TPA-NP1, the short-lived component of 95 ps can be assigned to PIET between donor triphenylamine and acceptor naphthalimide units (Fig. 6), which shows a fast charge separation and a thermally activated back reaction. PIET plays a major role in the fluorescence quenching of the naphthalimide moiety.

For an isolated chromophore without covalent bonding, the luminescence yield, η°, for NP when excited at 410 nm is given by

$$\eta^\circ = k_r{}^\circ/(k_r{}^\circ + k_{nr}{}^\circ), \tag{2}$$

where $k_r{}^\circ$ is radiative decay rate, and $k_{nr}{}^\circ$ is the non-radiative decay rate, both for an isolated molecule. When TPA is incorporated into NP, the yield, η, of the star-shaped compound TPA-NP1 is, assuming that the quenching is mostly due to photo-induced charge transfer (shown in Fig. 6), given by

$$\eta = k_r/(k_r + k_{nr} + k_q) = k_r/(k_r + k_{nr} + k_{et} + k_{bet}), \tag{3}$$

where k_r is the radiative decay rate, k_{nr} is the non-radiative decay rate, and k_q is the photo-induced electron transfer rate for the TPA-NP1 system. If considering that the luminescence quenching of the naphthalimide moiety in TPA-NP1 mostly results from photo-induced electron transfer, k_r can be assumed to be $k_r{}^\circ$. As indicated in Table 1, the luminescence yield, η, for TPA-NP1 is much smaller than η° ($\eta = 0.052\eta^\circ$). Since the luminescence lifetime of NP shows that $1/(k_r{}^\circ + k_{nr}{}^\circ)$ is about 9.32 ns in CH_2Cl_2, the lifetime data for TPA-NP1 is calculated to 0.48 ns (9.32×0.052), which is consistent with the determined average lifetime for TPA-NP1 (0.4 ns).

It should be pointed out that the occurrence of PIET from TPA to naphthalimide in the TPA-NP system is from the imide side of naphthalimide to the naphthalene unit, which is exactly supplement to the previous report by de Silva.[15] It was demonstrated that the naphthalimide chromophore is only unidirectional electron transfer, that is, only from the 4-position of naphthalimide to the naphthalene unit.[15] If considering that the unidirectional ET for the naphthalimide is unambiguously established, it's hard to elucidate the phenomenon observed here, i.e. strongly fluorescent quenching in the system of TPA-NP. As discussed above, one reason to be explained is based on the triphenylamine unit, which has a quite low oxidation potential and a strong electron donating tendency. In TPA-NP, the spacer between the imide side and the nitrogen is a benzene bridge, not a single carbon bond. Two possibilities, both the specifically low oxidation of TPA and the benzene bridge, contribute to the occurrence of such a very rare opposite PIET from the imide side to the naphthalene unit, which was well elucidated in our thermodynamic and transient fluorescence study. From this point of view, the model of TPA-NP is an unprecedented example for studying the unexpected PIET direction for the naphthalimide moiety.

Conclusion

A novel series of bipolar star-shaped naphthalimide derivatives (TPA-NP) were synthesized with triphenylamine as a core and the chromophores at the rims. Upon combining steady-state and transient fluorescence measurements, it is shown that there exist two possible processes, or effects, on the emission of the naphthalimide moiety: Förster singlet energy transfer and photo-induced electron transfer (PIET). The fluorescence decay of the naphthalimide moiety in the system of TPA-NP exhibits two contribution components with different lifetimes, in which the relatively short-lived fluorescent lifetime corresponds to PIET from the triphenylamine unit to the naphthalimide moiety. The existence of strong fluorescence quenching for the naphthalimide moiety bonded to the triphenylamine unit was observed. Especially for TPA-NP1 and TPA-NP2, quenching of the naphthalimide moiety reached as high as 95% in both cases of direct excitation (400 nm) and indirect excitation (310 nm). Such a strongly fluorescent quench of the naphthalimide moiety in the TPA-NP systems mostly results from PIET between the triphenylamine (donor) and naphthalimide units (acceptor). It is believed that the two possibilities, both the specifically low oxidation of TPA and the benzene bridge, can be attributed to the occurrence of such very rare opposite PIET from the imide side of naphthalimide to the naphthalene unit. Our studied model suggests that the luminescence quenching induced by possible through-bond PIET should be desirably considered when incorporating a triphenylamine unit to a chromophore for designing bipolar or star-shaped emitters.

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