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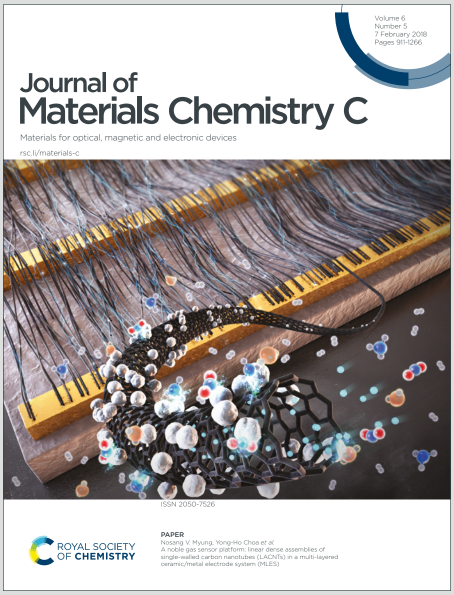

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Novel Side-chain Alternative Copolymer Combined FRET and DRET with Large Pseudo-Stokes Shift and Polarity-sensitive Fluorescent Behavior

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Abstract: a novel alternative copolymer incorporating tetraphenylethene (TPE) and naphthalimide (NI) into the styrene and maleic anhydride as side chains was designed and synthesized. Attributed to the TPE units acting both as emissive donor in aggregation state and dark donor in solution, this copolymer possessed fluorescence resonance energy transfer (FRET) and dark resonance energy transfer (DRET) processes from TPE to NI, so it kept emissive whether in solution or aggregation state, and fluorescence intensity of NI was increased obviously than it was excited directly without energy transfer. Additionally, the alternative copolymer displayed impressive pseudo-Stokes shift as large as 215 nm in aggregation state, which was larger than all other reported systems combined FRET and DRET. Lastly, we found that this alternative copolymer exhibited interesting polarity-sensitive fluorescent behaviors in different polarity environment, and these behaviors were considered to be the result of the combined effects of polarity-sensitivity, energy transfer and solubility.

Introduction

Fluorescent molecules were applied successfully in various fields, such as chemosensor and cell-imaging for their unique advantages like high sensitivity and easy visibility.[1-5] However, most of them exhibited relatively small Stokes shifts inducing serious self-quenching which limited the development of fluorescent materials.[6-7] Over the decades, fluorescence resonance energy transfer (FRET) strategy provided a useful solution for the small Stokes shifts problem.[7-8] An efficient FRET process was based on a close enough distance(1-10 nm) between donor and acceptor , and a large overlap between the emission spectrum of donor and the absorption spectrum of acceptor, so that FRET-based materials can produce large pseudo-Stokes shifts by constructing donor-acceptor pairs.[9-11] Whereas most of reported FRET systems employed emissive chromophore as donor, may lead to fluorescence leaking or background influence which was harmful for the applications of FRET materials.[12-13] Recently, Chang and co-workers developed a novel dark resonance energy transfer (DRET) strategy using low quantum yield fluorophores as dark donor to construct resonance energy transfer process.[14] It was successful to avoid fluorescence leaking or background influence induced by emissive donor. Moreover, DRET donor-acceptor pairs had large pseudo-Stokes shifts and showed high efficiency of energy transfer. [15-16] The mechanism of DRET was believed as that the quenching rate of dark donor through intramolecular-motion channel was slower quantitatively than the rate of resonance energy transfer between donor and acceptor.[14]

Aggregation-induced emission (AIE) effect reported by Tang's group provided an excellent strategy to overcome the aggregation-caused quenching (ACQ) effect of fluorescent molecules caused by π-π stack.[17] Typical AIE-gens, such as tetraphenylethene (TPE) and diphenylacrylonitrile, have a unique feature that it was emissive in aggregation state but was dark in solution. This unique feature is attributed to the restriction of the intramolecular motion or other quenching channels.[18-21] Taking advantage of this uniqueness, some scientists employed AIE-gens as emissive donors or acceptors to construct FRET materials which can be applied in aggregation state.[22-24] Lately, as dark donors, AIE-gens were combined with other fluorescent acceptors. Serdar Atılgan and co-workers developed a significate design of molecular that TPE, an AIE-donor, and BODIPY, a traditional fluorescent acceptor, were linked by a long alkyl chain.[25] It was the first work to introducing AIE-gen as a dark donor for constructing DRET pair. Interestingly, since TPE acted as emissive donor in aggregation state and dark donor in solution, this donor-acceptor pair which showed both FRET and DRET features. Similarly, Yang’s group reported a series of molecular， in which diphenylacrylonitrile were connected with BODIPY. [26] And the author concluded that the DRET and FRET processes probably were a normal phenomenon for AIE-BODIPY pairs. It was worth to notice that both above-mentioned two works reported large pseudo-Stokes shifts over 190 nm.

Compared with small-molecule materials, the polymer materials had excellent advantages such as good processing performance, film-forming ability and thermal stability, so more and more FRET pairs were introduced into copolymer materials.[27-36] However, FRET side-chain alternative copolymers rarely were reported to date. Considering the dependency of FRET efficiency on the distance between donor and acceptor, theoretically, it would be a good strategy to increase energy-transfer efficiency of FRET polymers by constructing side-chain alternative copolymer, in which donor and acceptor were introduced as side chain next to each other. In this work, we designed and synthesized a fluorescent copolymer P(TPE-alt-NI) combining DRET and FRET, in which tetraphenylethene (TPE)

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and naphthalimide (NI) were incorporated into the styrene and maleic anhydride as side chains (see Figure 1). This unique construction was designed for developing a fluorescent polymer materials with effective energy transfer whether in solution or aggregation state, and producing a large pseudo-Stokes shift to avoid self-quench and background influence. And this copolymer was endowed with polarity-sensitivity by the NI chromophores, so that its fluorescent behavior was changed with different solution polarity. Moreover, to investigate their own inherent fluorescence property of TPE or NI unit in polymer and to compare with the bi-chromophore copolymer, two copolymers P-TPE and P-NI which only contained TPE or NI fluorophore were synthesized too. We believe that the novel copolymer combining DRET and FRET with large pseudo-Stokes shift and polarity-sensitivity could provide a new strategy for the design of fluorescent polymer materials.

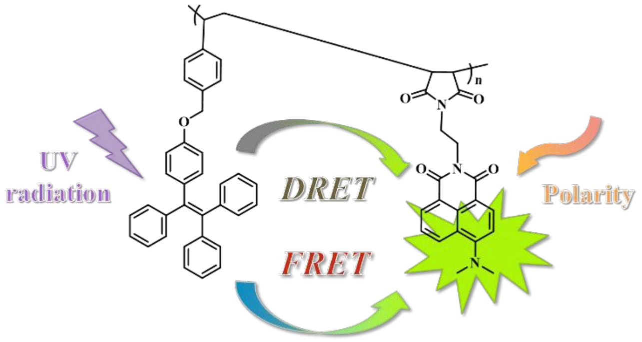


Figure 1. Schematic illustration of the resonance energy transfer process and polarity-sensitivity of P(TPE-alt-NI).

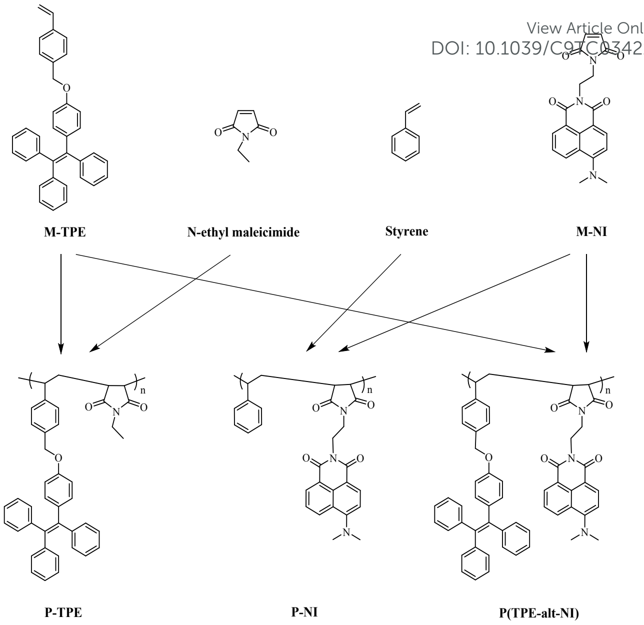
Results and Discussion

Molecular characteristics of the monomers and copolymers

As shown in Scheme 1， the chemical structures of the monomers and copolymers and corresponding polymerization were depicted. The detailed synthetic procedures of the monomers were summarized in supporting information. The molecular structures of these monomers and copolymers were confirmed by ^{1}H NMR spectroscopy (see Figure S1 and S2). The characteristic resonance peaks located at 5.2–6.6 ppm corresponding to the vinyl groups of these monomers had completely disappeared after polymerization, and other chemical shifts of each proton agreed well with their expected structures, indicating that these monomers were successfully introduced to the resulting copolymers P-TPE, P-NI and P(TPE-alt-NI). The conversion rates of monomers for polymerization, the number-average molecular weights (Mn) and polydispersity index (PDI) of copolymers characterized by gel permeation chromatography (GPC) were summarized in Table 1.

Thermal properties of the copolymers

The decomposition temperature (Td) and the glass transition temperature (Tg) of the copolymers were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) respectively. These results were summarized in Table 1 and the curves were depicted in Figure 3. As bi-chromophore copolymer, the Td and Tg of P(TPE-alt-NI) were at medium value between the corresponding value of P-TPE and P-NI as expected. And all of them showed good thermal stability.



Scheme 1. The chemical structures of the monomers and copolymers and polymerization procedures

UV-Vis absorption properties

The photophysical properties of M-TPE, M-NI, P-TPE, P-NI and P(TPE-alt-NI) in THF solution were investigated in detail, and the concentrations of each chromophore were set as 1×10^{-5} M. These results were summarized in Table 2. And the UV-Vis absorption spectra of M-TPE, M-NI and their alternative copolymer P(TPE-alt-NI) in THF were shown in Figure 2. The absorb band with a maximum at 317 nm was characteristic of the TPE chromophore, whereas absorb band with a maximum at 410 nm was corresponded to the NI chromophore, and it was observed that the two major absorb band of P(TPE-alt-NI) were similar to its two monomers at 311 nm and 417 nm respectively. This result reflected that the TPE unit and NI unit were introduced to the alternative copolymer successfully. And as shown in Figure S3, the absorption spectra of P-TPE and P-NI in THF were similar with respective fluorescent monomers too.

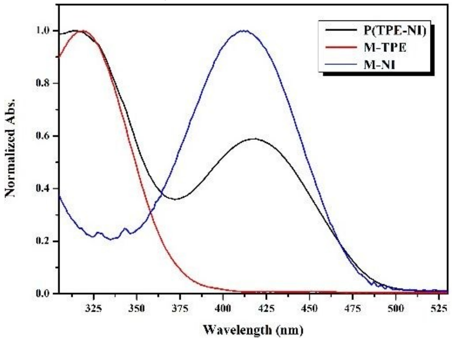


Figure 2. UV-Vis absorption spectra of M-TPE, M-NI and P(TPE-alt-NI) in THF solution (1×10^{-5} M).

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Table 1. Molecular characteristics, thermal properties of copolymers, and conversion rates of monomers.

	Mn （×10^4）	PDI	Tg（℃）	Td（℃）	Conversion rates (%)
P-TPE	6.47	3.82	164	384	89
P-NI	4.86	2.21	216	429	91
P(TPE-alt-NI)	5.75	2.50	180	402	83

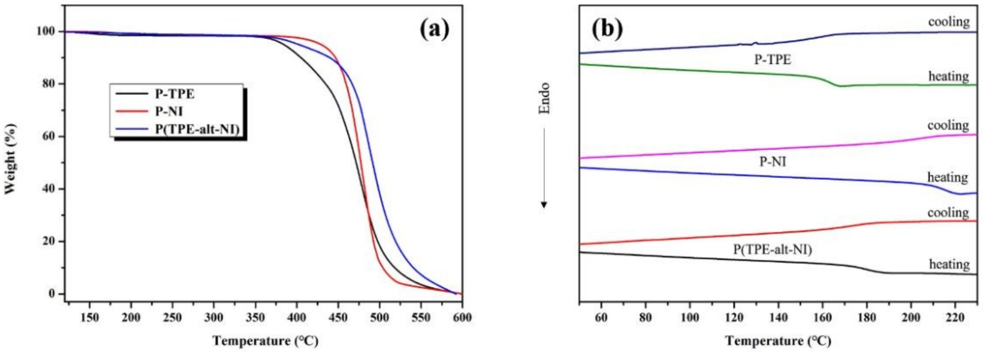

Figure 3. (a) TGA curves of copolymers at a heating rate of 20℃/min and (b) DSC curves of the copolymers during the first cooling and second heating scans at a rate of 10℃/min.

AIE & ACQ effect of P-TPE and P-NI

The fluorescence properties of copolymers which only contained single chromophore were measured respectively by changing fraction of water (f_w) in THF solution. The results were depicted in Figure S4. When excited at 320 nm, P-TPE showed no emission in pure THF. However, with the increasing f_w from 10 to 90%, the emission peak at ~470 nm corresponding to the TPE units was observed, and the fluorescence intensity was enhanced gradually. This result clearly comfirmed the AIE effect of P-TPE. Whereas, when excited at 430 nm, P-NI exposed an emission peak at ~530 nm in pure THF, but when the f_w was increased, its fluorescence was quenched obviously owing to the ACQ effect of NI chromophores in P-NI.

Resonance energy transfer processes

Considering that an efficient overlap between the emission spectrum of donor and the absorption spectrum of acceptor was the necessary condition for resonance energy transfer, we compared the emission spectrum of P-TPE with the absorption spectrum of P-NI. As shown in Figure 4, the overlap region from 388 nm to 590 nm meant it was suitable to employ the TPE chromophore as donor and the NI chromophore as acceptor in a resonance energy transfer process.

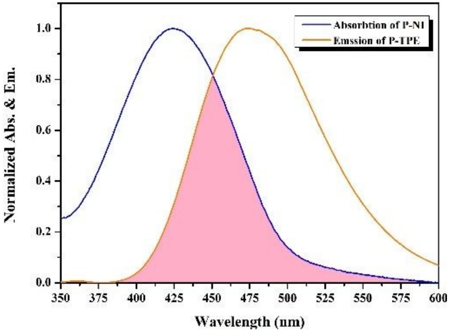

Figure 4. Overlap between the emission spectrum of P-TPE and the absorption spectrum of P-NI.

To investigate the DRET process from the TPE units to NI units in P(TPE-alt-NI), the fluorescence spectra of the P-TPE, P-NI and P(TPE-alt-NI) excited at 320 nm and 430 nm in THF solution were measured respectively. As shown in Figure 5a, the fluorescence spectra of the P-TPE, P-NI and P(TPE-alt-NI) excited at 320 nm in THF were compared. Because of the AIE effect of TPE chromophore, the P-TPE showed no emission when it was excited at 320 nm in solution. And because the NI chromophore could not be excited efficiently at 320 nm, the P-NI only demonstrated a weak emission. However, when the alternative copolymer P(TPE-alt-NI) was excited at the absorption wavelength of TPE (320 nm), very intensive fluorescence corresponding to NI fluorophore at 517 nm was observed. This result indicated distinctly there was a DRET process, in which TPE unit acted as dark donor and NI unit acted as an emissive acceptor, and it produced an impressive pseudo-Stokes shift as 206 nm which was larger than all other reported DRET systems. As depicted in Figure 5a, the fluorescence intensity of P(TPE-alt-NI) excited at 320 nm was higher obviously than P-NI excited at 430 nm, even though their quantum yields were similar (see Table 2). It may be attributed to the overlap between the emission spectrum of TPE and the absorption spectrum of NI. This overlap made the DRET process more effective than a single wavelength excitation of acceptor. And the alternative construction of this copolymer induced an easy energy transfer process, in which every TPE unit as donor was close enough to every near-by NI units as acceptor. Moreover, NI units were separated to each other by TPE units, so the concentration-quenching of NI fluorophore was reduced. Based on these unique features including non-emissive donor, strong fluorescence intensity and large pseudo-Stokes shift, the novel alternative copolymer may provide a new strategy for the development of fluorescent materials without fluorescence leaking, background influence and self-quenching.

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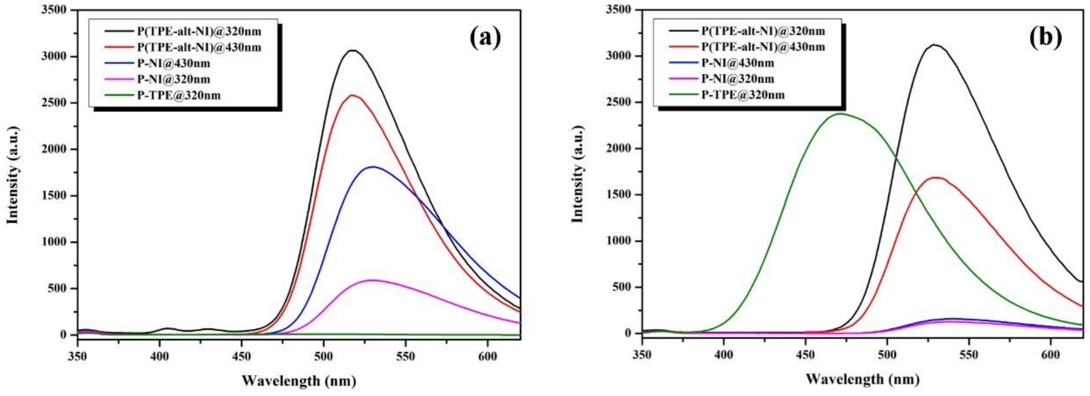

Figure 5. (a) Emission spectra of P(TPE-alt-NI) and P-NI excited at 320 nm and 430 nm respectively, and P-TPE excited at 320 nm, in 1×10^{-5} M THF solution. (b) Emission spectra of P(TPE-alt-NI) and P-NI excited at 320 nm and 430 nm respectively, and P-TPE excited at 320 nm, in 1×10^{-5} M water/THF(9:1).

Table 2. Photophysical properties of monomers and copolymers as 1×10^{-5} M in THF solution.

	λ_{abs} (nm)^{a}	λ_{em} (nm)^{b}	Φ_F (%)^{c}	Stokes shift (nm)^{d}
M-TPE	317	--	--	--
M-NI	410	514	--	104
P-TPE	318	--	--	--
P-NI	424	530	12.3	96
P(TPE-alt-NI)	311, 417	517	11.2	206

a. Absorption peak value of M-TPE, M-NI, and P(TPE-alt-NI) measured in THF solution. b. Emission maximum wavelength measured in THF solution. M-TPE, P-TPE and P(TPE-alt-NI) were excited at 320 nm, and M-NI and P-NI was excited at 430 nm. c. Fluorescence absolute quantum yields measured in THF. λex = 430 nm for P-NI and 320 nm for P(TPE-alt-NI). d. Stokes shift of M-NI or P-NI and pseudo-Stokes shift of P(TPE-alt-NI).

In addition, upon 430 nm UV, P(TPE-alt-NI) in solution demonstrated a stronger emission than P-NI too. In this case, TPE chromophore in P(TPE-alt-NI) did not be excited while only NI chromophore did, so energy transfer did not occur. It meant that the emission caused by NI chromophore excited directly instead of energy transfer from TPE. This phenomenon could be explained as the before-mentioned “separated effect” of alternative construction of this copolymer too.

Considering the AIE-active of TPE, it is feasible to act as an emissive donor of FRET process in aggregation state. To study the fluorescent behavior of the alternative copolymer P(TPE-alt-NI) in aggregation state, the photophysical properties P-TPE， P-NI and P(TPE-alt-NI) in water/THF (9:1) were investigated in detail, and these results were summarized in Table 3. As shown in Figure 5b, the AIE-active P-TPE excited at 320 nm showed a strong 472 nm emission in aggregation state. And P-NI, upon 430 nm, only exhibited a red-shifted weak emission as a result of the close stacking of NI fluorophores. As for P(TPE-alt-NI), when excited upon the TPE’s absorption wavelength (320 nm), this copolymer showed a 528 nm emission corresponding to NI units instead of TPE units. It was indicated clearly that an efficient FRET process occurred between emissive TPE units and emissive NI units in the aggregative P(TPE-alt-NI). According to the amount of quenching of the donor chromophores, the efficiency of FRET could be calculated.[38] The whole disappearance of emission of TPE donor with increased emission of NI acceptor indicated nearly 100% efficiency of FRET in the alternative copolymer. Additionally, similar as in solution, the fluorescence intensity of aggregative P(TPE-alt-NI) based on FRET was higher than which excited directly at 430 nm, and It may be attributed to alternative construction of the copolymer as we before-mentioned in this paper. And the red-shifted emission of aggregative NI fluorophores led to a larger pseudo-Stokes shift of P(TPE-alt-NI) as 215 nm.

Moreover, when aggregative and dissolved P(TPE-alt-NI) excited both at 320 nm， their quantum yields were similar (see Table 2 and Table 3), and as shown in Figure 5a and 5b, their fluorescence intensity were approximate and both were higher obviously than aggregative P-NI excited at 430 nm. The emission of aggregative P(TPE-alt-NI) was a result of comprehensive effect including “separated effect” and FRET process. As the precondition, the “separated effect” reduced the π-π stacking of NI chromophores to avoid ACQ effect, and then the FRET process could have an emissive NI acceptor so that P(TPE-alt-NI) exhibited emission in the aggregative polymer. When λ_{ex} = 430 nm, the Φ_F of P-NI in aggregation state as 7.34% was lower than the Φ_F of P(TPE-alt-NI) in aggregation state as 15.3%, so this result indicated that the “separated effect” avoided the ACQ effect of NI chromophores successfully.

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Table 3. Photophysical properties of 1×10^{-5} M P-TPE, P-NI and P(TPE-alt-NI) in water/THF (9:1).

	λ_{ab} (nm)^a	λ_{em} (nm)^b	Φ_F (%)^c	E (%)^d	Stokes shifts (nm)^e
P-TPE	318	471	9.87	--	153
P-NI	431	540	7.34	--	109
P(TPE-alt-NI)	313,421	528	10.2	≈100	215

a. Absorption peak value measured in water/THF (9:1). b. Emission maximum measured in water/THF (9:1). P-TPE and P(TPE-alt-NI) were excited at 320 nm, and P-NI was excited at 430 nm. c. Fluorescence absolute quantum yields measured in water/THF (9:1). λex = 430 nm for P-NI and 320 nm for P-TPE, and P(TPE-alt-NI). d. Efficiency of fluorescence resonance energy transfer. e. Stokes shifts for P-TPE and P-NI, and pseudo-Stokes shift for P(TPE-alt-NI).

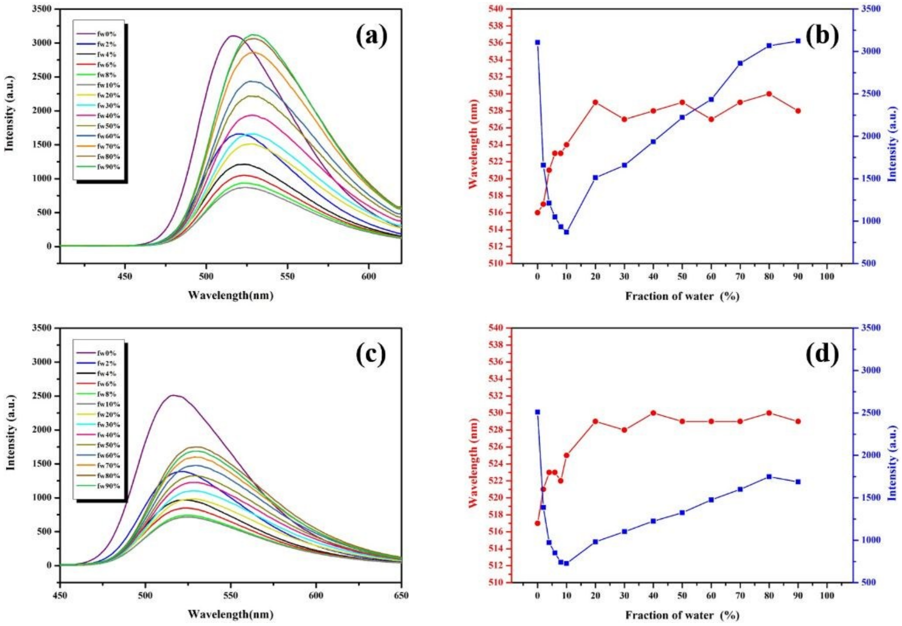

Figure 6. Emission spectra of 1×10^{-5} M P(TPE-alt-NI) in different ratio water/THF excited at 320 nm (a) and 430 nm (c). Variation of PL intensity and wavelength maximum of 1×10^{-5} M P(TPE-alt-NI) in different ratio water/THF excited at 320 nm (b) and 430 nm (d).

Polarity-sensitive fluorescent behavior

4-Amino-1, 8-naphthalimide derivatives were polarity-sensitive attributed to the intramolecular charge transfer (ICT) between the electron-donating 4-amino substituent and the electron-withdrawing imide ring. [39-41] With increasing solvent polarity, the emission of them would became weak and red-shifted. Pavel Kucheryavy and co-workers investigated the effect of solvent polarity on the energy of S1 State in 4-(N, N-dimethylaminonaphthalimide (Me_2N-NI). [39] As shown in Scheme S2, they found that the 4-substituent of Me_2N-NI in the ground-state was at a small angle relative to the naphthalene ring, whereas in the optimized excited-state geometry, the 4-substituent was at 90° angle, and this twisted excited state was unstable in nonpolar solvent. When polarity of solvent was increased, the twisted excited state of Me_2N-NI became stable so that the energy of S1 State of Me_2N-NI became lower, which resulted a weak and red-shifted emission.

In previous measurement of this paper, the ACQ effect of P-NI had been verified by investigating emission intensity of P-NI in different ratio of water/THF (see Figure S4b). To study the effect of solvent polarity on P-NI, further fluorescence measurement of P-NI in different fraction of water or n-heptane in THF (f_w or f_n) was investigated in detail. The fluorescence intensity both decreased gradually as the addition of poor solvents as expect (Figure S5a and S5c). The quenched fluorescence was caused by aggregative NI chromophores in P-NI. However, comparing the Figure S5b and S5d, it was worth noticing that the decrease of fluorescence intensity with increasing f_n was slower and less than which with increasing f_w, and the red-shift trend of maximum emission wavelength was dramatic when water was added into THF rather than the gradual process with increasing f_n. These phenomenon were attributed to the polarity-sensitive NI chromophores in P-NI. As we know, water is a polar solvent whereas n-heptane is non-polar, with the increasing f_w, the whole polarity of mixed solvent became stronger, in contrast, the increasing f_n made the polarity of mix solvent decrease. In a word, different solvent polarity induced the changed emission from the polarity-sensitive NI chromophores. As a result, P-NI showed different fluorescent behaviors in water/THF and n-heptane/THF.

Then we investigated fluorescent behavior of P(TPE-alt-NI) excited at 320 nm with different f_w in THF solution, and these results were depicted in Figure 6a and 6b. In the initial stages of adding water, the fluorescence intensity of P(TPE-alt-NI) excited showed a dramatic decline, however, after the f_w reached 10%, the emission became enhanced gradually, and when the f_w reached 90%, its intensity even returned to the initial level as in pure THF solution. This interesting phenomenon was considered to be the result of the combined effects of polarity-

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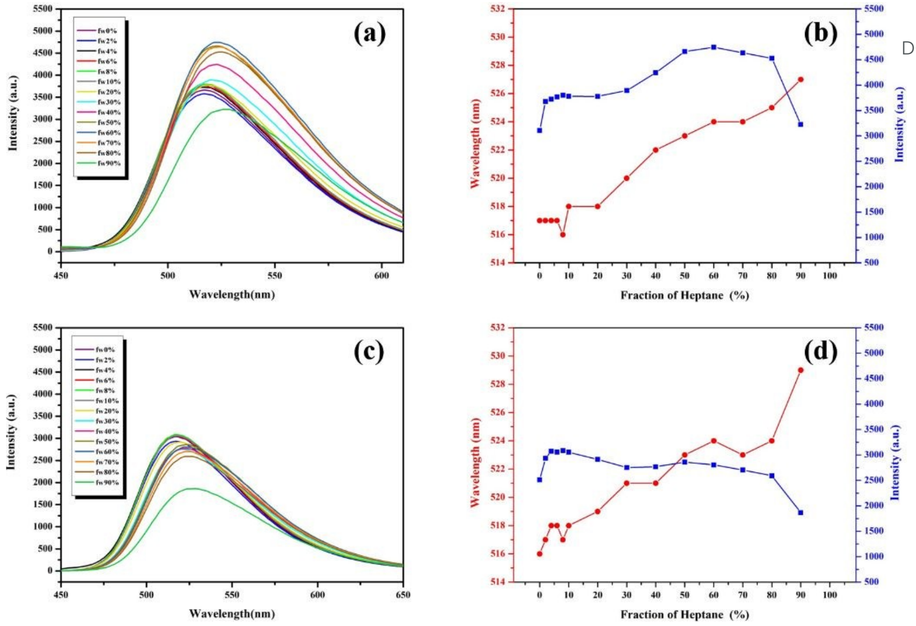

Figure 7. Emission spectra of 1×10^{-5} M P(TPE-alt-NI) in different ratio n-heptane/THF excited at 320 nm (a) and 430 nm(c). Variation of PL intensity and wavelength maximum of 1×10^{-5} M P(TPE-alt-NI) in different ratio n-heptane/THF excited at 320 nm (b) and 430 nm (d).

sensitivity, energy transfer and solubility. At the beginning, P(TPE-alt-NI) was excited by 320 nm in pure THF solution, in which happened a DRET process between TPE units as dark donor and NI units as emissive acceptor. When water just was added in the THF solution of P(TPE-alt-NI), the dramatically increased polarity of solution induced the decreased fluorescence of polarity-sensitive NI chromophores. But after the f_w reached 10%, the effect of solvent polarity against NI chromophores did not increase anymore. Meanwhile, the added water as a poor solvent made P(TPE-alt-NI) became more and more aggregative, as a result, the distance between TPE donor and NI acceptor became closer so that the emission was enhanced by an easier energy transfer. On the other hand, the closer aggregation of the copolymer shielded the effect of solvent polarity. Lastly, because NI units were separated to each other by TPE units, so that the ACQ effect of NI fluorophore was avoided partly. Until the f_w reached 90%, these above reasons leaded to the originally quenched fluorescence gradually returned to the initial level as in pure THF. It was worth noticing that as the degree of aggregation increased, the AIE-active TPE chromophore turned from a dark donor to an emissive donor, so the DRET in P(TPE-alt-NI) switched to the FRET gradually throughout the whole process of addition water.

For comparison, fluorescent behavior of P(TPE-alt-NI) with different f_w in THF excited at 430 nm was investigated. As shown in Figure 6c and 6d, the fluorescence intensity first declined and then increased gradually as the water added, but until the end it never returned to the initial level as in pure THF. And in each water fraction, the fluorescence intensity of P(TPE-alt-NI) excited at 430 nm was weaker than which upon 320 nm. This phenomenon was a result of the absence of FRET or DRET when P(TPE-alt-NI) was excited at 430 nm, and indicated that the acceptor’s emission from resonance energy transfer process was stronger than direct excitation upon acceptor’s absorption wavelength.

Compared with addition of water， it was different that the fluorescence behavior of P(TPE-alt-NI) excited at 320 nm or 430 nm in different ratio of n-heptane/THF, but still was a result of the combined effects of polarity-sensitivity, energy transfer and solubility too. As shown in Figure 7a and 7b, initially, P(TPE-alt-NI) excited by 320 nm in pure THF solution, in which happened a DRET process between TPE and NI units, so this solution exposed 517 nm emission corresponding to NI chromophores. When f_n was increased from 0 to 10%, the decreased solvent polarity made the emission of NI chromophores enhanced gradually. Then f_n was increased from 10 to 20%, the upward trend of fluorescence intensity became flat, this because the effect of polarity against NI did not increase anymore. After the f_n reached 20%, the distance between TPE donor and NI acceptor in aggregated P(TPE-alt-NI) became closer, so the emission was enhanced continuously by the easier energy transfer. But when f_n was increased 60 to 90%, the fluorescence intensity dropped to the initial level as in pure THF, because the very compact aggregation of NI units caused emission quenching. For comparison, fluorescent behavior of P(TPE-alt-NI) excited at 430 nm in different f_n was investigated. As shown in Figure 7c and 7d, the fluorescence intensity increased gradually as the decreased solvent polarity when n-heptane just added. But after the f_n reached 10%, the fluorescence intensity declined continuously until the f_n reached 90%. This result indicted that without energy transfer, the emission of NI chromophores in P(TPE-alt-NI) excited at 430 nm would be easier to quenched by aggregation.

Furthermore, as shown in Figure 7b and 7d, the curve of red-shifted emission wavelength of P(TPE-alt-NI) with increasing f_n was different with which with increasing f_n. We believe that the red-shifted emission of P(TPE-alt-NI) with increasing f_w and f_n

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was a combined result of the solubility and polarity of solvent. As poor solvent, both of increasing water and n-heptane contents induced a more aggregative polymer coil， in which the π-π stacking of NI chromophores produced a red-shifted emission of polymer. Of course, the effect of polarity of solvent also played an important role, especially in the initial stages of process. As shown in Figure 6, when water just was added in the THF solution of P(TPE-alt-NI), the polarity of solvent was increased dramatically, and at the same time, the polymer coil became aggregative as the added poor solvent, so the two reasons together induced a large degree of red-shifted emission. After the f_w reached 20%, the polymer became condense enough so that the effect of solvent polarity was shielded and the π-π stacking of NI chromophores reached the limit, as a result, the emission wavelength was no longer red-shifted basically. As for the case of increasing f_n (see Figure 7b and 7d), the decreased polarity of solvent was no good for red-shift of emission, but at the same time， n-heptane as poor solvent made polymer coil became more aggregative, so the effect of solvent polarity was shielded gradually and the π-π stacking of NI chromophores induced a continued red-shifted emission of polymer (the process of aggregation with increasing f_n may be slower than the case with increasing f_w for different anti-solubility of the two poor solvents). In a word, solubility and polarity of solvent induced together the red-shifted wavelength of emission, in which polarity mainly worked in the initial stages whereas solubility led the whole red-shift process.

Lastly, an interesting phenomenon was observed that the fluorescence intensity of P(TPE-alt-NI) in 90% water/THF and 90% n-heptane/THF were similar (see Figure S6). We implied that when the fraction of poor solvent reached 90%, the aggregate of P(TPE-alt-NI) had already been compact both in water/THF and n-heptane/THF solution, so the influence of solvent polarity was weak, and the poor solubility became the dominant influent factor of fluorescence intensity. When P(TPE-alt-NI) in 90% f_w or 90% f_n were excited, their similar compact degree of aggregated P(TPE-alt-NI) induced similar fluorescence intensity.

Conclusion

A novel alternative copolymer incorporating tetraphenylethene (TPE) and naphthalimide (NI) into the styrene and maleic anhydride as side chains was designed and synthesized. Systematic optical investigation showed that this copolymer kept emissive whether in solution or aggregation state associated with fluorescence resonance energy transfer (FRET) and dark resonance energy transfer (DRET) processes from TPE to NI, because the TPE unit can act as emissive donor in aggregation state and dark donor in solution, and the alternative structure increased the efficiency of energy transfer and avoided the ACQ of NI. Particularly, this copolymer displayed an impressive pseudo-Stokes shift as large as 215 nm in aggregation state. Moreover, this copolymer exhibited interesting polarity-sensitive fluorescent behaviors in different ratio water/THF and n-heptane/THF solvent, attributed to the combined effects of polarity-sensitivity, energy transfer and solubility. We believe that this work would be helpful for the study of resonance energy transfer, and provide a new strategy for the development of polarity-sensitive fluorescent polymer materials.

Experimental section

Materials

N-Boc-Ethylenediamine (96%), trifluoroacetic acid (99%), 4-bromine-1,8-naphthal anhydride (98%), maleic anhydride (99%), 4-hydroxybenzophenone (99%), benzophenone (99%), zinc power (99%), titanium tetrachloride (99%), and 1-(chloromethyl)-4-vinylbenzene (99%) were purchased from Energy Chemical Co. and were used directly. Tetrahydrofuran (AR, Kermel Co., 99%) was refluxed over metal sodium and distilled out before use. Azodiisobutyronitrile (AIBN, AR, 95%) was purchased from Xilong Chemical Co., and further purified by recrystallization from ethanol. N, N-dimethylformamide (DMF, AR, 99%), n-heptane (AR, 99%) and Acetone (AR, 99%) were purchased from Tianjin Fuyu Fine Chemical Co. And copper (II) sulfate pentahydrate (AR, Guangdong Guanghua Sci-Tech Co., 99%), acetic anhydride (AR, Kelong Co., 99%) were used directly without further purification.

Instrumentation and measurement

Number-average molecular weights (Mn) and polydispersity index (PDI) of the copolymers were measured by a gel permeation chromatography (GPC, WATERS1515) instrument calibrated with standard polystyrenes. THF was used as eluent and the flow rate was 1.0 mL min^{-1} at 35℃. The ^{1}H nuclear magnetic resonance (NMR) spectra of monomers and copolymers were measured by Bruker ARX400 MHz spectrometer. The decomposition temperature (Td, defined as temperature that weight percentage loss 5 wt%) of polymers were measured by thermogravimetric analysis (TGA) Q50 with a scanning rate of 20℃ min^{-1} under N_2 atmosphere. The glass transition temperature (Tg) of copolymers was measured by a TA Q10 differential scanning calorimetry (DSC) instrument operating with a scanning rate of 10℃ min^{-1} on heating and cooling process. The transition temperatures and enthalpies were calibrated using standard materials (indium and zinc). The absorption spectra of monomers and copolymers in different ratio of THF/water or THF/n-heptane were taken on an Agilent spectrum Carry 100 spectrophotometer. The fluorescence spectra of monomers and copolymers in different ratio of water/THF or n-heptane/THF were taken on a PTIQm400 luminescence spectrometer. The fluorescence absolute values were obtained using an Edinburgh FLS920 Fluorescence Spectrometer with integrating sphere. In all measurements of photophysical property, the concentrations of each chromophore were set as 1×10^{-5} M.

Polymerization

Equimolar amount of two monomers (M-TPE and N-ethyl maleicimide for P-TPE, M-NI and styrene for P-NI, M-TPE and M-

NI for P(TPE-alt-NI), AIBN (0.01 molar equivalent of monomers), chlorobenzene (2.3 mass equivalent of monomers) were placed in a dry glass tube, then the tube was degassed by several freeze–pump–thaw cycles and sealed under vacuum. Polymerization was carried out at 75 ℃ for 4 h. After terminated by putting the tube into an ice–water mixture, the polymer solutions were diluted with THF and precipitated into methanol to obtain the target polymers of P-TPE, P-NI and P(TPE-alt-NI).

Conflict of interest

There are no conflicts to declare.

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Keywords: aggregation-induced emission • alternative copolymers • dark resonance energy transfer (DRET) • FRET • solvent effects

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