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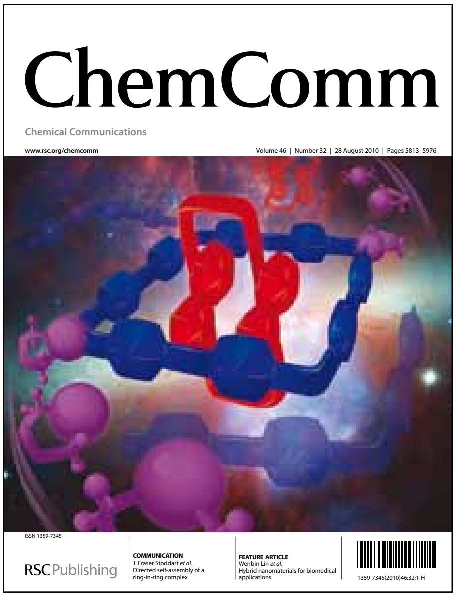

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ARTICLE TYPE

Initiator-lightened Polymers : preparation of end-functionalized polymers by ATRP and their intramolecular charge transfer and aggregation-induced emission

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A simple strategy to prepare AIE polymers is invented using an AIE initiator for atom transfer radical polymerization. The dual photoresponse by intramolecular charge-transfer and luminogen aggregation of the initiator is well-realized and even enlarged after polymerization, due to the linkage of polymer chains.

Molecules equipped with aggregation-induced emission (AIE) have gained serious attention because of potential applications in optoelectronic devices, chemosensors, and bioprobes.[1a-1g] Tang's group and others have successfully designed and synthesized various small AIE active molecules, such as TPE[1e, 2a-b] and HPS.[2c] Fabrication of small AIE-equipped molecule for practical applications, however, remains a challenge, largely because of the reliance on expensive equipment and complicated processes for fabrication. In light of those problems, high molecular weight polymers have been considered as candidates. High molecular weight polymers possess high-quality film, and can be prepared using simple processing techniques, such as spin-coating. Until now, few AIE-active polymers have been developed; most cases have been developed by introducing a monomer with AIE moiety into the main or side chain.[2a-b, 2d] However, it is difficult to confirm the exact number of AIE moiety in the copolymer chain. If a single chromophore anchored on a polymer chain, as well as its AIE effect, could be preserved, it would be an extremely interesting method with which to obtain an AIE active polymer. A pertinent question thus becomes how to effectively realize the design of such a process. Further, the question of whether a single chromophoric unit in a polymer chain could induce sufficient changes in the properties of the polymer remains important. One efficient existing method involves the use of controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) technologies.[3a-3c]ATRP, which was first proposed by Matyjaszewski and Sawamoto, etc., has emerged as a feasible technique for obtaining well-defined polymers.[4a-b] Considering the above information, in this study, an AIE active initiator was introduced at the end of a polymer chain; subsequently, its impact on the AIE effect both before and after polymerization was studied.

In the present research, we designed and synthesized an intramolecular charge transfer (ICT) and an AIE dual active initiator, TPP-NI (Fig. 1a). This molecule originated from a pyrazoline chromophore; it possesses an electron donor (dimethylamino), and an electron acceptor (l,8-naphthalimide). The DFT calculation showed that the distortion angle of the naphthalimide and pyrazole rings reached 58° (see Fig. 1b). Such a structure could hamper the effective π-π stacking between the dye molecules, a process that enables the molecules to efficiently emit in the condensed phase. The photoluminescence (PL) of TPP-NI was quenched in DMF solution, but was recovered by the following method: using poor polar solvent, such as toluene; and producing nanoaggregation.

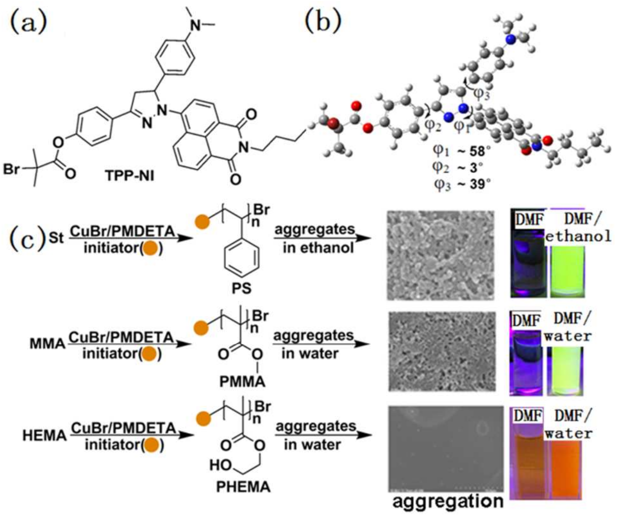

Figure 1 (a) Formula of TPP-NI; (b) Optimized ground-state geometry of initiator with B3LYP/6-31G* in gas phase; (c) Scheme of synthetic routine of polymers.

When TPP-NI was used as an ATRP initiator, the regular monomers, such as styrene (St), methyl methacrylate (MMA), and 2-hydroxyethyl methacrylate (HEMA) (with different hydrophilic properties) could be respectively polymerized in a moderate condition. These α-end functionalized polymers (PS, PMMA, and PHEMA) were well dissolved in DMF solution, but tended to aggregate when water or ethanol was added. Interestingly, the molecules were almost nonemissive in pure DMF solution; yet an abrupt increase of PL intensity and quantum yield was observed when the polymer chains aggregated. The emission intensity was stronger than that in the respective DMF solution by the following, according to solution: PS in DMF/ethanol mixture, 155-fold; PMMA in DMF/water mixture, 65-fold; and PHEMA in DMF/water mixture, 10-fold. Further, the PL intensity of PHEMA dramatically enhanced with the increased acidification of the solution; specifically, PL intensity was about 7-fold higher than it was in DMF/water. We thus attempted to elucidate the AIE mechanism differences herein.

The existence of ICT was confirmed by measuring the absorption and emission spectra of the initiator and PS in three different polar solvents (DMF, THF, and toluene). In the DMF solution of the initiator, there are two prominent bands at 330 nm and 475 nm, which can be ascribed to a localized aromatic π-π* transition, and an ICT character of l, 8-naphthalimide, respectively. When the polarity of the solvent decreased, an ICT character blue-shift was observed (460 nm and 451 nm in THF and toluene, respectively). Initiator emission was almost quenched in DMF (549 nm), was moderate in THF (525 nm), and was highest in toluene (507 nm) (Fig. 2a). The obvious increase in the stokes' shift with the increasing polarity of solvents (2,449 cm^{-1} in toluene, 2,691 cm^{-1} in THF, and 2,838 cm^{-1} in DMF) further verified the ICT character of the excited state in our system. Generally, ICT states can be effectively stabilized in polar media such as DMF and water, and this is not benefitial to emission in our system.[54-b] These phenomena were observed in PS solution, indicating that polymer ICT was well-preserved. Using different solvents, we could turn on the emission of the TPP-NI molecule and its end-functionalized polymers.

We also studied the initiator and polymers AIE effect in a DMF/water (ethanol) mixture; the absorption spectra of the initiators have been presented and discussed in detail in the supporting information.

The absorption behaviors were similar for the three PS with different molecular weights (see Fig. S4-3, S4-4, and S4-5). The absorption spectra of PSa with various fractions of ethanol have been shown in Fig. 2b. With added ethanol, the light scattering effect of the nanoaggregates could be observed gradually.[6] The polymer chain formed different sizes of nanoparticles in accordance with different ethanol volumes added (Fig. S7-2). Specifically, with increased ethanol content, smaller nanoparticles were obtained accordingly.

The absorption pattern of PMMA was similar to that of PS, but the aggregate degree was relatively lower (Fig. 2c). However, the absorption pattern of PHEMA was different; light scattering was not observed, even when the water content was increased to 80 % (Fig. 2d). This was likely due to the strong interaction between PHEMA and polar solvents and the fact that its aggregation degree was the lowest.

Compared to that of DMF solution, the effect of water on initiator emission was obvious. When the water fraction was about 60 %, λem was red shifted, the intensity ratio (I/I_0) reached a maximum value of 13, and the fluorescent quantum yield (QY) was 1.4 % (Fig. 3a).

The PS emission was studied using a DMF/ethanol mixture. The weak emission band of PS in DMF solution was at about 545 nm; this was blue shifted by about 30 nm in comparison to the weak emission band of the initiator. This could likely be attributed to different intramolecular and intermolecular interactions in the polymer chains. With the addition of ethanol into the DMF solution, the emission band of PSa was slightly blue shifted, and intensity increased gradually after 50 % ethanol content was reached. The highest intensity was reached in 99 % ethanol, a value that was 155-fold higher (Φ_F = 19 %) than that in the pure DMF (Φ_F < 1 %). The emission intensities of PSb and PSc were 98-fold (Φ_F = 15 %) and 72-fold (Φ_F = 13 %) larger than those in pure DMF, respectively (Fig. 3b). Additionally, normal PS with BABrP doped in could not achieve the AIE effect, because the BABrP still dissolved in ethanol when PS aggregated. It may be explained that the chromophore anchored at the end of polymers was easily twisted in the best emissive form by a rigid matrix. Moreover, the QY of PSa was the highest, although AIE fluorphore content was the lowest due to its largest Mw. It may be proposed that the stronger wrapping of polymer chains not only protected the initiator from solvent to avoid quenching, but that it also amplified the AIE effect. Therefore, the emission amplification of polymers was mainly ascribed to two facts that the aggregated polymer protected initiator from solvent to avoid quenching and made it in an emissive configuration.

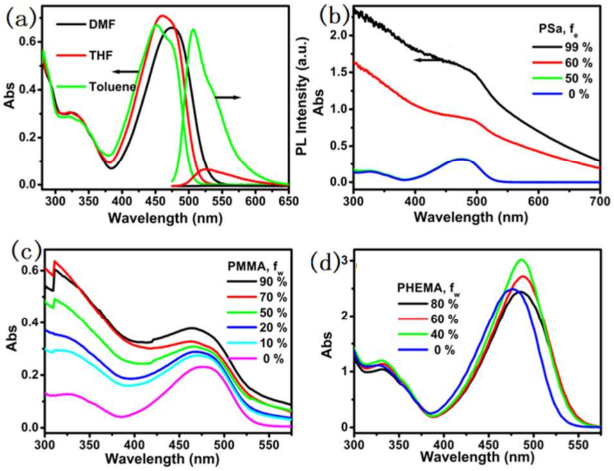

Figure 2 (a) Absorption and emission spectra of initiator in different solvents; (b) Absorption spectra of PSa with the composition of the DMF/ethanol mixture; (c) Absorption spectra of PMMA with the composition of the DMF/water mixture; (d) Absorption spectra of PHEMA with the composition of the DMF/water mixture.

It should be noted that PS films prepared by spin-coating were highly emissive under UV light irradiation. In particular, the QYs of PS films were unexpectedly high, and increased as molecular weight increased (PSa was 48 %, PSb was 42 %, and PSc was 35 %). This interesting result may make them good candidates for optical chips.

The PMMA showed similar AIE effects compared to those of

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PS. However, the AIE amplification effect in PMMA was weaker than it was in PS because the polarity of PMMA is stronger than that of PS, and the wrapping of the fluorphore is less effective.

The AIE phenomenon was much weaker in the PHEMA system. When water content was increased to 90 %, the intensity was only 10-fold higher than it was in the DMF solution; it exhibited a weak emission at 570 nm, which was similar to that of the initiator. This was because the polar PHEMA chain could not easily hamper initiator ICT, and obvious emission quenching was thus observed.

The pressing question of how to recover the emission remains. When sulfuric acid was added into the DMF solution, a gradual increase of emission intensity was observed; it reached a maximum when the pH value was about 1. However, only a slight enhancement of emission intensity could be observed in similar PS and PMMA systems, respectively (see Fig. S4-10). We tentatively propose the following reasons for the AIE mechanism observed in PHEMA: (i) although the dimethylamino (DMA) group in TPP-NI is a well-known pH sensor in solution, TPP-NI itself could not dissolve in water, and the pH effect was nearly unobservable; (ii) because the polarities of PS and PMMA nanoparticles are low, there are few DMA groups anchored on the particle surface, and the enhancement of emission is limited; and (iii) hydrogen bonds between HEMA's hydroxyl group and the water molecule are destroyed in acid solution, and thereafter the polymer aggregates. However, the polarity of PHEMA causes the exposure of more dimethylamino groups on the surface, and the effect of the pH value is amplified.

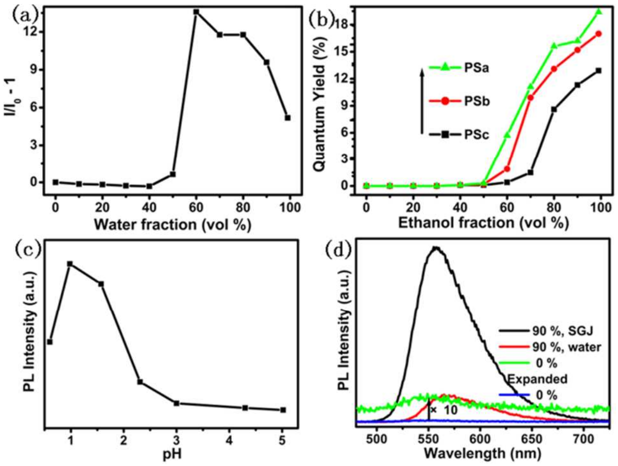

Figure 3 (a) Change in the relative PL intensity (I/I_0) of initiator in the DMF/water mixture. I_0 = PL intensity in DMF solution. Concentration: 25 uM; excitation wavelength: 467 nm; (b) Change in QYs of PS in the DMF/ethanol mixture; (c) Change in emission intensity of PHEMA in DMF at different pH values; (d) Emission spectra of PHEMA in DMF, DMF/water mixture, and SGJ solution, respectively.

These characteristic differences of PHEMA make it more attractive for future practical applications. We have utilized PHEMA as a PL sensor in simulated gastric juice (SGJ) solution. The λem of PHEMA in SGJ solution was blue shifted by almost 10 nm, but the intensity was much higher than those in the DMF (70-fold) and DMF/water mixtures (7-fold) (Fig. 3d). PHEMA could be applied in an oral drug-delivery system, both as an optical sensor and as a supplemental carrier to encase the hydrophobic drug molecules effectively in the stomach.

In summary, an AIE-active initiator is introduced to the terminal of a polymer chain and enables the regular polymers to emit dramatically. Although the AIE effect of this small molecule is not distinctive, the obvious amplification of polymers emission is observed. It should partly attributed to the wrapping and coiling of flexible hydrophobic chains. The AIE effect is originated from initiator TPP-NI, but amplified through polymer chains or tuned by polarity of the polymer side chains. The prepared polymers exhibit not only the AIE effect of the terminal group but also the property of the polymer chains, such as easy fabrication. In particular, the PHEMA shows a pH-optical sensitive phenomenon, which is not obvious in both small molecules and regular polymers without such a fluorphore. We believe that such a method is promising in preparation of AIE polymers and studying the morphology of classical polymers using fluorescence.

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Notes and references

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1(a) M. M. Cai, Z. Q. Gao, X. H. Zhou, X. P. Wang, S. F. Chen, Y. Z. Zhao, Y. Qian, N. E. Shi, B. X. Mi, L. H. Xie and W. Huang, *Phys. Chem. Chem. Phys.,* 2012, 14, 5289; (b) Z. Q. Guo, W. H. Zhu and H. Tian, *Chem. Commun.,* 2012, 48, 6073; (c) J. A. Ho, H. C. Chang and W. T. Su, *Anal. Chem.* 2012, 84, 3246; (d) T. Y. Han, X. Feng, B. Tong, J. B. Shi, L. Chen, J. G. Zhi and Y. P. Dong, *Chem. Commun.,* 2012, 48, 416; (e) C. H. Li, T. Wu, C. Y. Hong, G. Q. Zhang and S. Y. Liu, *Angew. Chem. Int. Ed.* 2012, 51, 455; (f) V. Bhalla, V. Vij, A. Dhir and M. Kumar, *Chem. Eur. J.* 2012, 18, 3765; (g) S. Kim, Q. D. Zheng, G. S. He, D. J. Bharali, H. E. Pudavar, A. Baev and P. N. Prasad, *Adv. Funct. Mater.* 2006, 16, 2317.
2 (a) L. Tang, J. K. Jin, A. Qin, W. Z. Yuan, Y. Mao, J. Mei, J. Z. Sun and B. Z. Tang, *Chem. Commun.*, 2009, 4974; (b) A. J. Qin, L. Tang, J. W. Y. Lam, C. K. W. Jim, Y. Yu, H. Zhao, J. Z. Sun and B. Z. Tang, *Adv. Funct. Mater.* 2009, 19, 1891; (c) Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.,* 2011,40, 5361.(review); (d) H. G. Lu, F. Y. Su, Q. Mei, X. F. Zhou, Y. Q. Tian, W. J. Tian, R. H. Johnson and D. R. Meldrum, *J. Polym. Sci. Part A: Polym. Chem.,* 2012, 50, 890.
3 (a) P. Theato, *Angew. Chem. Int. Ed.*, 2011, 50, 5804; (b) S. Nojima, Y. Ohguma, K. I. Kadena, T. Ishizone, Y. Iwasaki, K.Yamaguchi, *Macromolecules* 2010, 43, 3916; (c) P. Y. Gu, C. J. Lu, Q. F. Xu, G. J. Ye, W. Q. Chen, X. M. Duan, L. H. Wang and J. M. Lu, *J. Polym. Sci. Part A: Polym. Chem.,* 2012, 50, 480.
4 (a) J. Qiu and K. Matyjaszewski, *Macromolecules* 1997, 30, 5643; (b) J. Ueda, M. Atsuyaman, M. Kamigaito and M. Sawamoto, *Macromolecules* 1998, 31, 557.

5 (a)C. J. Fahrni, L. C. Yang, D. G. VanDerveer, *J. Am. Chem. Soc.,* 2003, 125, 3799; (b) J. Cody, S. Mandal, L. C. Yang, C. Fahrni, *J. Am. Chem. Soc.,* 2008, 130, 13023.
6 Y. Liu, S. M. Chen, J. W. Y. Lam, P. Lu, R. T. K. KwoK, F. Mahtab, H. S. Kwok and B. Z. Tang, *Chem. Mater.,* 2011, 23, 2536.