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Sensitive and reliable detection of glass transition of polymers by fluorescent probes based on AIE luminogens

Suping Bao,[a] Qihua Wu,[a] Wei Qin,[b] Qiuling Yu,[a] Jing Wang,[a] Guodong Liang,*[a] Ben zhong Tang*[b]

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Glass transition of polymers is an immensely-used yet less-understood phenomenon concerning dynamics of polymer chains in bulks or in confined surroundings, which dictates directly their performances in engineering sectors. Monitoring glass transition or dynamics of polymers is hampered by the lack of facile but robust methodologies. Herein, we developed a sensitive, reliable and straightforward approach for detection of glass transition of polymers using fluorescent probes based on aggregation induced emission (AIE) luminogens. Fluorescence emission of polymers doped with AIE luminogens including tetraphenylethene (TPE) or its derivatives showed a sensitive response to glass transition of polymers. Sensitivity of fluorescence to glass transition could be optimized by increasing TPE loading. Fluorescence intensity of TPE-doped polymers dropped as much as 25 folds with raising temperature in the investigated range. The temperature dependence of fluorescence intensity gave rise to straightforward determination of glass transition of polymers. Moreover, it is worth mentioning that simply mixing AIE luminogens with polymers, rather than covalently labeling, is applicable due to AIE characteristics of the probes. This facilitated significantly measurements. Given the significant advantages of AIE luminogens as probes, including high and tunable sensitivity, immune to aggregation, facile operation and simple data processing, fluorescence techniques based on AIE luminogens offer a new access to investigation of glass dynamics of polymer chains in confined space.

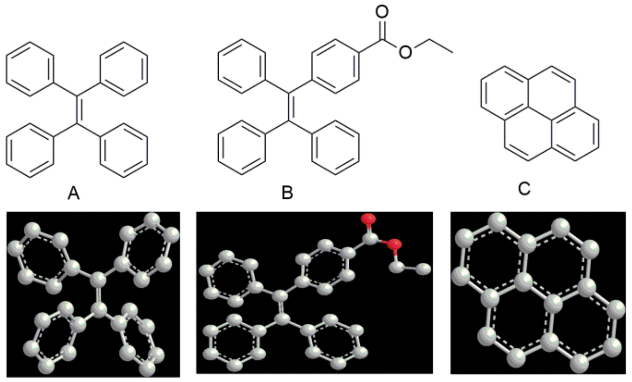
Introduction

Glass transition is a reversible transition between brittle glassy state and soft rubbery state in amorphous polymers, which is accompanied by significant variations in mechanical properties, viscosity, thermal-expansion coefficient, specific heat, and so on.[1, 2] For instance, elastic modulus of polymers drops by several orders of magnitude when they convert from glass state into rubbery state with raising temperature.[3] Glass transition temperature (T_g) of polymers at which glass transition takes place, dictates directly their service temperature. For example, plastics must be used at temperature below T_g, while rubbers are used at temperature above T_g. Determining T_g of polymers, particularly onset temperature of glass transition is extremely crucial for their applications in engineering sectors. Moreover, investigating glass transition or dynamics of polymer chains is essential for fundamentally understanding performances of polymers, especially at interface or surface with applications in adhesion, biological, solar cells, drug release.[1, 2]

A number of techniques have been used to determine glass transition of polymers including dilatometry, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and so on. Dilatometry measures volume change of polymers during glass transition. Dilatometry is simple and facile, but suffers from poor accuracy.[4] DMA, mainly used for engineering materials, determines glass transition by testing viscoelastic properties of polymeric materials. DMA requires massive samples (a few grams).[5] Compared with the formers, DSC has been immensely used due to relatively small amount of samples needed (a few milligrams) and ease of operation.[6, 7] However, some of technical issues prevent thermal-based DSC from accurate and reliable determination of T_g of polymers including baseline drift and fluctuation (see Electronic Supporting Information, ESI). Moreover, DSC measurements give a temperature range that glass transition occurs. Different definitions of glass transition temperature make numeric results of T_g very different from each other (ESI).

With the rapid extension of applications of polymers in emerging fields including lithography, solar cells and selective membranes, new requirements must be met to determine the glass transition of polymers for special applications. For instance, to determine T_g of polymers confined in limited space such as polymer films, the approaches mentioned above fail to work, and new methods with high sensitivity must be developed because only a small amount of materials is available for measurements.[8-13] Fluorescence technique is emerging as a promising approach for investigating glass transition due to high sensitivity.[14-22] Determination of T_g by fluorescence is pioneered by Torkelson.[23-26] Pyrene (Scheme 1) was used as a fluorescent probe to label polymers. The variation of fluorescence emission of pyrene-labeled polymers during glass transition of polymers allowed for determination of T_g of polymers. Although this technique is applicable to polymer films, the transition is ambiguous and plausible likely due to weak fluorescence.[23] Even worse is that fluorescence intensity can not be enhanced by increasing concentration of probes, which leads to aggregation of probes and consequent aggregation-caused quenching (ACQ) of fluorescence. This resulted in limited sensitivity of fluorescence to glass transition of polymers. Moreover, covalently labeling of pyrene into polymers involved fussy synthetic procedures, and it was not applicable to existing polymers. All these limitations restrict its further applications.

In contrast to ACQ probes, aggregation-induced-emission (AIE) luminogens emit intense light in solid state based on mechanism of restriction of intramolecular motions (RIM).[27, 28] Aggregation or vitrification of AIE luminogens activates the RIM process, which consequently results in strong fluorescence emission either in aggregation state or in monomer state.[29, 30] Taking the advantage of AIE luminogens, the fluorescence intensity of polymers doped with AIE dyes can be efficiently enhanced by increasing probe loading without need to avoid aggregation of probes. This promises enhanced sensitivity of fluorescence to glass transition of polymers. Herein, we reported sensitive and reliable detection of glass transition of polymers using fluorescent probes based on AIE luminogens. A class of typical AIE luminogens including tetraphenylethene (TPE), ethyl 4-(1,2,2-triphenylvinyl)benzoate (TPE-C2) (Scheme 1) and 2-(tetraphenylethoxy)ethanol (TPE-C2OH) were utilized as fluorescent probes to dope polymers. Taking advantages of high quantum yield and AIE characteristics of TPEs, all the issues encountered by the methods mentioned above such as poor accuracy, big amount of samples needed, poor sensitivity, and so on, can be addressed. Glass transition of polymers can be detected in a sensitive, reliable and straightforward manner. Given significant advances in synthesis of AIE dyes in recent years,[31-34] fluorescence techniques based on AIE luminogens as probes offer new opportunities for fundamentally understanding glass transition or dynamics of polymer chains in confined surroundings.



Scheme 1 Chemical structure and ball-rod modelling of TPE (A) and TPE-C2 (B) as well as pyrene (C).

Results and discussion

Amorphous polystyrene (PS) with narrow molecular weight distribution was selected as a model polymer. TPE was utilized as fluorescence probe due to AIE characteristics, high quantum yield and ease of synthesis.[31, 32] TPE-doped polystyrene (PS/TPE) emitted intense blue light upon UV radiation (365 nm) (Fig. 1). X-ray diffractometry (XRD) was used to characterize the dispersion of probes in polymer matrix. No diffraction peaks from TPE were detected for PS/TPE, suggesting that TPE was uniformly dispersed in the PS matrix without formation of large aggregates, likely due to resembled chemical constitutions and good miscibility between PS and TPE.

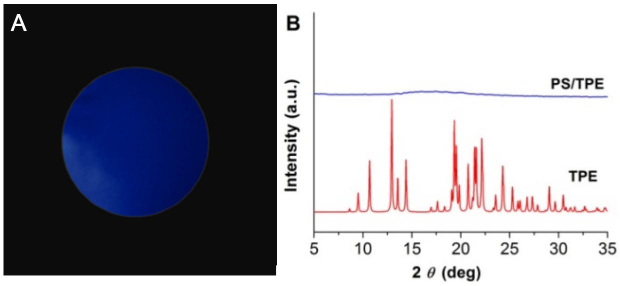


Fig. 1 (A) Fluorescent image of PS/TPE under UV radiation (365 nm) and (B) XRD curves of PS/TPE (containing 1.0 wt% TPE) and TPE.

Glass transition of pristine PS and PS/TPE was determined by using differential scanning calorimetry (DSC) (Fig. S1, ESI). Glass transition of PS took place in a temperature range of 78 ºC – 98 ºC centered at 89.5 ºC (T_g). Doping PS with small amount of TPE did not affect noticeably glass transition of the polymer matrix.

Fluorescence spectra of PS/TPE at various temperatures were presented in Fig. 2. PS/TPE emitted strong blue light (470 nm) at room temperature. With raising temperature, the intensity of fluorescence decreased. Plots of fluorescence intensity at 470 nm against temperature showed that the fluorescence intensity dropped linearly and drastically with increasing temperature. The straight line levelled off when temperature approached 80 ºC. Thereafter, fluorescence intensity decreased slightly with further raising temperature. The transition temperature is determined to be 80 ºC, in the temperature range determined by using DSC (78 ºC– 98 ºC), close to the onset temperature (78 ºC). The possible reason is that in glassy state TPE molecules are embedded in rigid polymer matrices. The intramolecular motions (*i.e.* rotation, vibration, torsion, bending, and so on) of phenyl rings of TPE are restricted to some extent. The energy of excited state is annihilated through radiation decay, and thus TPE emits efficiently. When polymers are in rubbery state, intramolecular motions of TPE are activated due to movement of polymer segments and significantly increased free volume in polymer matrices. The intramolecular motions consume the energy of excited state. This leads to weak fluorescence emission of TPE in rubbery state of polymers.[27, 28]

Moreover, it was interesting that the fluorescence intensity of PS/TPE decreased more drastically at low temperature, implying that fluorescence of PS/TPE is more sensitive to thermal expansion below T_g rather than segmental movements above T_g. This is rational because size of phenyl rings of TPE is a few angstroms (< 3 Å) (Scheme S1, ESI). To restrict the motions (*i.e.* rotation, vibration, torsion, bending, and so on) of phenyl rings of TPE, they have to be compacted into a small space of a few angstroms (< 3 Å). In another word, subtle change in free volume of polymer matrix takes significant effect on intramolecular motions of TPE. This leads to an obvious decrease in fluorescence intensity at temperature below T_g. When temperature reaches T_g, mobility of polymer segments is significantly enhanced. Restriction on intramolecular motions of TPE molecules further decreases due to drastically increased free volume, resulting in further decreased fluorescence intensity.

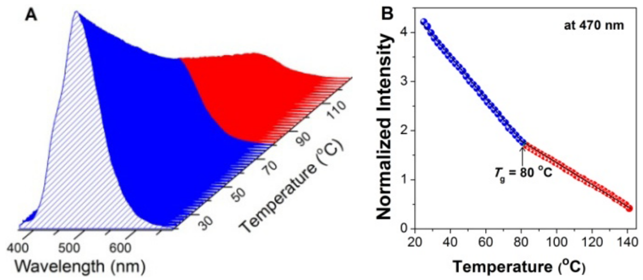


Fig. 2 (A) Fluorescence spectra of PS doped with 0.1 wt% TPE at various temperatures and (B) fluorescence intensity at wavelength of 470 nm as a function of temperature normalized to 110 ºC. Excitation: 350 nm.

We checked reproducibility of fluorescence spectra of PS/TPE at various temperatures. Fluorescence spectra of PS/TPE switching between 40 °C (<T_g) and 110 °C (>T_g) were presented in Fig. 3. Fluorescence spectra of PS/TPE at 40 °C showed a distinct emission peak at 470 nm, while the emission was much weaker at 110 °C. The fluorescence emission was capable of reversibly switching by repeatedly altering temperature between 40 °C and 110 °C. This revealed that PS/TPE was stable for repeated thermal treatments.

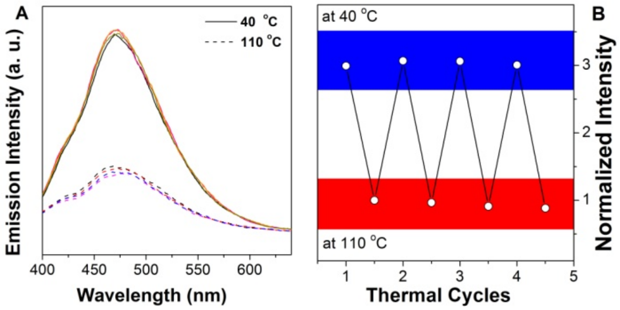


Fig. 3 (A) Fluorescence spectra of PS doped with 0.1 wt% TPE at 40 °C and 110 °C and (B) fluorescence intensity (470 nm) at 40 °C and 110 °C. Excitation: 350 nm.

Improving sensitivity of fluorescence to glass transition is possible. We investigated the effect of TPE loading on the fluorescence of PS/TPE, as shown in Fig. 4. Compared with PS doped with 0.1 wt% TPE, PS doped with 1.0 wt% TPE showed more distinct glass transition (Fig. 4A). The fluorescence intensity dropped as much as 25 folds (from 5.8 to 0.23), much larger than that for 0.1 wt% TPE (10 folds, from 4.2 to 0.4, Fig. 2). Interestingly, glass transition temperature was still determined to be 80 ºC. This demonstrated that it was possible to improve the sensitivity of fluorescence to glass transition by simply increasing probe loading without affecting numeric results of T_g. This is inaccessible to ACQ probes such as pyrene, where increasing concentration of probes leads to the formation of excimers or aggregates and consequent fluorescence quenching.[35-37] For AIE luminogens such as TPE, aggregation favors emission, and thus allows enhancing fluorescence intensity by increasing AIE luminogen loading. This promises enhanced sensitivity of fluorescence to glass transition of polymers. Monitoring glass transition of polymers at low TPE loading is also feasible. We detected glass transition of PS at low TPE loading of 0.05 wt%. Glass transition was recognized at 80 ºC again. This reveals that T_g can be reliably obtained regardless of TPE loading used, which is crucial for practical measurements.

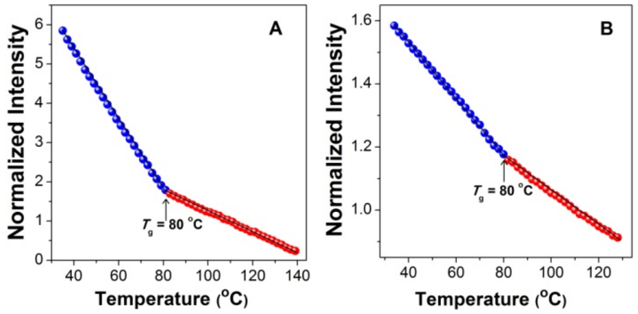


Fig. 4 Fluorescence intensity at 470 nm of PS doped with 1.0 wt% TPE (A) and 0.05 wt% TPE (B) as a function of temperature. Excitation: 350 nm.

TPE can be readily modified to adapt polymers with various constitutions and polarities. Taking another model polymer of poly(methyl methacrylate) (PMMA) as an example, TPE derivate with a polar tail (TPE-C2, Scheme 1B) was synthesized for improved miscibility between PMMA and probes. Fluorescence spectra of PMMA doped with 0.1 wt% TPE-C2 (PMMA/TPE-C2) at various temperatures were shown in Fig. 5. PMMA/TPE-C2 emitted intense blue light (476 nm) at room temperature. Fluorescence intensity at 476 nm decreased linearly and drastically with raising temperature. The straight line bent downwards when temperature reached 103 ºC. DSC results of PMMA showed that glass transition of PMMA occurred in a temperature range of 100 ºC – 119 ºC centered at 110 ºC (Fig. S2, ESI). The transition temperature determined using TPE-C2 as a fluorescent probe (103 ºC) was close to the onset temperature of glass transition by using DSC.

TPE derivatives (TPE-C2 and TPE-C2OH, respectively) were also used to dope PS. Fluorescence spectra of PS doped with TPE-C2 and TPE-C2OH were shown in Fig. 6 and Fig. 7, respectively. The transition temperature was determined to be 80 ºC, identical to the value using TPE as a fluorescent probe. This illustrated that TPE based AIE luminogens were universal fluorescent probes for monitoring glass transition of polymers. Significant advances in synthesis of AIE dyes in recent years enrich fluorescent probes used for monitoring glass transition of polymers.[31, 32]

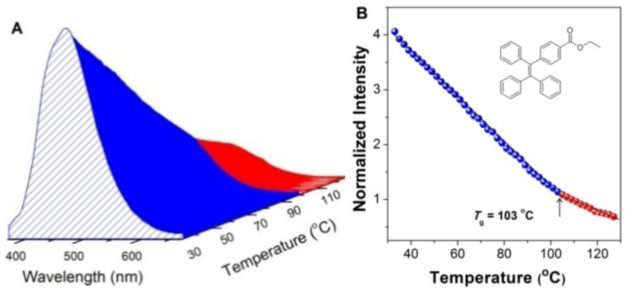


Fig. 5 (A) Fluorescence spectra of PMMA doped with 0.1 wt% TPE-C2 at various temperatures (B) fluorescence intensity at wavelength of 476 nm as a function of temperature normalized to 110 ºC. Excitation: 350 nm.

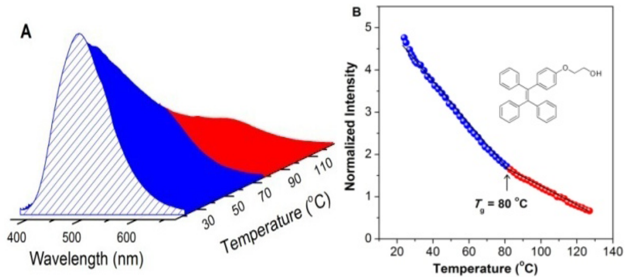


Fig. 6 (A) Fluorescence spectra of PS doped with 0.1 wt% TPE-C2OH at various temperatures (B) fluorescence intensity at wavelength of 476 nm as a function of temperature normalized to 110 ºC. Excitation: 350 nm.

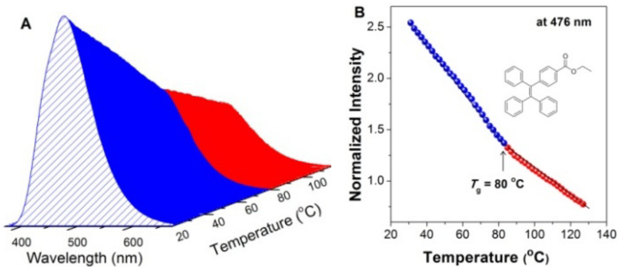


Fig. 7 (A) Fluorescence spectra of PS doped with 0.1 wt% TPE-C2 at various temperatures (B) fluorescence intensity at wavelength of 476 nm as a function of temperature normalized to 110 ºC. Excitation: 350 nm.

Torkelson and coworkers measured fluorescence spectra of pyrene-labeled PS at various temperatures.[23-26] They used temperature dependence of the ratio of the intensity of the third peak (386 nm) to the intensity of the first peak (375 nm) (I_3/I_1) of the fluorescence spectra to determine T_g of PS, as shown in Fig. 8. Compared with pyrene, TPE as probes possesses overwhelming advantages: (1) fluorescence intensity of TPE-doped polymers changed abruptly during glass transition, revealing that fluorescence of TPE-doped polymers was much more sensitive to glass transition of polymers. For example, fluorescence intensity varied as much as 25 folds (from 5.8 to 0.23) for TPE-doped PS in the temperature range investigated (Fig. 4A), while by 1.3 folds for pyrene-labeled PS (intensity of maximal peak varied from 1.0 to 0.8 in Fig. 8A). (2) Sensitivity of fluorescence of TPE-doped PS to glass transition can be optimized by increasing TPE loading. Taking the advantage of AIE characteristics, the fluorescence intensity of TPE-doped PS can be efficiently enhanced by increasing loading of TPE without avoiding aggregation of TPE.[27, 28] This is impossible for pyrene, which is a typical ACQ dye. (3) Immune to the aggregation of probes, it is not necessary to take complicated synthesis procedures to label polymers with probes to avoid the aggregation of probes. Simply mixing polymers with TPEs promises sensitive and reliable detection of glass transition of polymers. This facilitates significantly measurements. Moreover, TPE presents a single emission peak, much simpler than pyrene. Temperature dependence of fluorescence spectra of TPE-doped polymers gives rise to straightforward determination of T_g without fussy calculation. In addition, TPE can be easily synthesized in high yields, and starting materials are cheap and easy to get.[31, 32] With all these advantages, TPE and its derivatives are excellent candidates of fluorescence probes for detecting glass transition or dynamics of polymer chains.

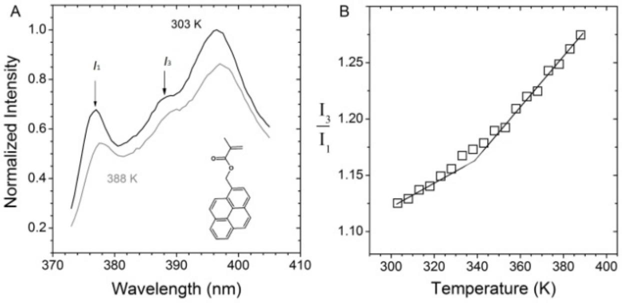


Fig. 8 (A) Fluorescence spectra of pyrene-labeled PS at various temperatures and (B) the ratio of intensities at the third and first peaks as a function of temperature. Reprinted with permission from ref 23.

Conclusions

In summary, we developed a sensitive, reliable and straightforward approach for detection of glass transition of polymers using fluorescent probes based on AIE luminogens. Fluorescence emission of polymers doped with tetraphenylethene (TPE) or its derivatives showed a sensitive response to glass transition of polymers. The sensitivity of fluorescence to glass transition can be optimized by increasing TPE loading. The fluorescent intensity of TPE-doped polystyrene deceased as much as 25 folds with raising temperature in the range investigated. Such temperature dependence of fluorescence intensity allowed for straightforward determination of glass transition of polymers. With significant advantages of AIE luminogens as probes including high and tuneable sensitivity, immune to aggregation, facile operation and data processing, ease of synthesis, and so on, fluorescence techniques based on TPEs offer new opportunities for monitoring glass transition or dynamics of polymer chains in confined space.

Experimental

Materials

Tetraphenylethene (TPE) and its derivates (TPE-C2 and TPE-C2OH) were synthesized according to protocols in literatures.[33, 34] benzophenone, 4-hydroxybenzophenone, pyridine, *n*-butyllithium and 4-bromobenzophenone were purchased from Sigma (China) without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Polystyrene (PS) with narrow polydispersity (M_n=10.2 kg/mol, PDI=1.09) was purchased from Aladdin Industrial Inc. Poly(methyl methacrylate) (PMMA) with narrow polydispersity (M_n=105 kg/mol, PDI=1.09) was purchased from Polymer Source Inc.

Characterization

Fluorescence spectra were recorded on a Steady State Spectrometer (Edinburgh Instrument Ltd, FLSP920) equipped with a temperature control system (Oxford instruments). To eliminate the interference of heating rates on the glass transition determination, heating rate was fixed at 1 ºC/min for all specimens. Fluorescence spectra were scanned every 1 min. X-ray Diffraction (XRD) measurements were performed using XRD diffractometer (D-MAX 2200 VPC) equipped with Ni-filtered Cu Kα radiation, having a wavelength of 0.154 nm. The diffractometer was scanned in 2θ range from 1.5 º to 50 º and the scanning rate used was 1.2 º min^{-1}. DSC measurement was carried out using a Perkin-Elmer DSC-7 Instrument under nitrogen atmosphere. Temperature was calibrated with indium prior to the test. Heating rate was set at 1 ºC/min.

Preparation of Polymers Doped with AIE Dyes

50 mg polymers and prescribed amount of AIE dyes were dissolved in 10 mL freshly-distilled THF with stirring to yield homogeneous solutions. The resulting solutions were cast onto clean quartz wafers. Polymer films with thickness of 100 µm were obtained after evaporation of solvent. The polymer films were annealed at 120 °C for 12 h in vacuum.

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Notes and references

[a] *DSAP lab, PCFM lab, GDHPPC lab, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China; E-mail: lgdong@mail.sysu.edu.cn*

[b] *HKUST-Shenzhen Research Institute, No. 9 Yuexing 1st RD, South Area, Hi-tech Park, Nanshan, Shenzhen, China 518057; Department of Chemistry, Institute for Advanced Study, Division of Biomedical Engineering and Institute of Molecular Functional Materials, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China; Guangdong Innovative Research Team, SCUT-HKUST Joint Research Laboratory, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China; E-mail: tangbenz@ust.hk*

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