

# Highly sensitive and selective fluorometric off–on $K^+$ probe constructed *via* host–guest molecular recognition and aggregation-induced emission†

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In this work, we integrated the concept of aggregation-induced emission (AIE) with the specific supramolecular recognition between  $K^+$  ions and crown ether moieties to develop more effective fluorometric  $K^+$  probes. We synthesized a novel crown ether-functionalized tetraphenylethene (TPE) derivative, TPE-(B15C5)<sub>4</sub>, *via* the thiol-ene click reaction of thiol-derivatized TPE, TPE-(SH)<sub>4</sub>, with maleimide-functionalized benzo-15-crown-5 (B15C5). In TPE-(B15C5)<sub>4</sub>, the TPE core and four outer B15C5 moieties serve as the AIE-active motif and supramolecular  $K^+$ -recognizing functionalities, respectively. TPE-(B15C5)<sub>4</sub> molecularly dissolves in THF with negligible fluorescence emission. As we have envisaged, upon  $K^+$  addition, TPE-(B15C5)<sub>4</sub> can be effectively induced to aggregate due to  $K^+$ -mediated cross-linking *via* the formation of  $K^+$ /B15C5 (1/2 molar ratio) molecular recognition complex in a sandwiched manner. This process is concomitantly accompanied with the turn-on of fluorescence emission *via* the AIE mechanism. Thus, TPE-(B15C5)<sub>4</sub> can serve as highly sensitive and selective fluorometric off–on  $K^+$  probes.

## 1. Introduction

Over the past decades, the exploration of novel detection strategies for the  $K^+$  ion has attracted significant interest due to its extremely important roles in various physiological activities and biological functions.<sup>1</sup> In comparison with other conventional analytical approaches, colorimetric and fluorometric  $K^+$  probes offer distinct advantages in terms of sensitivity, selectivity, fast response, and enhanced spatial and temporal resolution.<sup>2</sup> Until now, a variety of elegant optical  $K^+$  chemosensors and biosensors, either in an emission intensity-based or a ratiometric manner, have been developed by utilizing  $K^+$ -modulated photoinduced electron transfer (PET),<sup>1a,3</sup> photoinduced charge transfer (PCT),<sup>4</sup> or fluorescent resonance energy transfer (FRET) mechanisms.<sup>5</sup> The construction of small molecule-based fluorometric  $K^+$  probes typically relies on the molecular recognition between  $K^+$  ions and crown ether or cryptand hosts as they typically exhibit weak affinity with conventional heavy metal ion-binding ligands.<sup>2,6</sup>

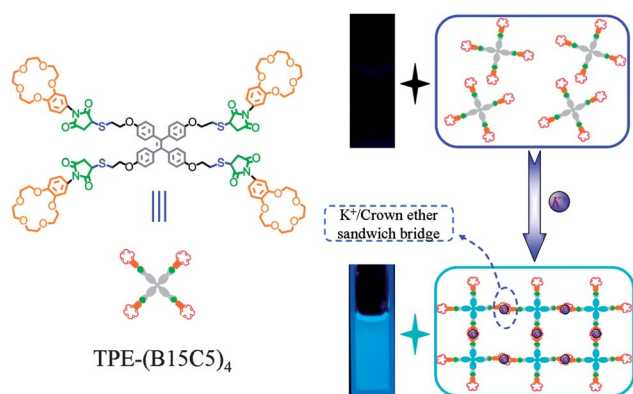
In addition to the mechanism of analyte-modulated conventional photophysical processes such as PET, PCT, and FRET,

recently, the concept of aggregation-induced emission (AIE)<sup>7</sup> or aggregation-induced enhanced emission (AIEE)<sup>8</sup> has emerged to be a potent and versatile strategy for fabricating novel types of fluorescent probes. Typical molecules exhibiting AIE features, such as tetraphenylethene (TPE), are non-emissive in molecularly dissolved state, whereas enhanced fluorescence emission was achieved when they are in the aggregated state. Tang *et al.*<sup>7,9,10</sup> has ascribed the AIE phenomenon to the restriction of intramolecular rotation (RIR) of fluorogenic molecules within aggregates, which effectively blocks the non-radiative energy dissipation pathways and favors the radiative decay of excitons. In the past few years, various AIE-based chemosensors and biosensors for analytes ranging from heavy-metal ions, thiols, explosive, carbohydrates, DNA, to proteins and enzymes have been developed.<sup>9–11</sup>

To the best of our knowledge, the AIE mechanism has been less exploited to develop fluorometric probes for  $K^+$  ions, which are expected to offer advantages such as high detection selectivity and sensitivity, low background interference, and enhanced imaging contrast. In this work, we further integrated the AIE concept with the specific supramolecular recognition between  $K^+$  ions and crown ether moieties, aiming for the facile development of more effective fluorometric  $K^+$  probes. We synthesized a novel crown ether-functionalized TPE derivative, TPE-(B15C5)<sub>4</sub>, *via* the thiol-ene click reaction<sup>12</sup> of thiol-modified TPE, TPE-(SH)<sub>4</sub>, with maleimide-functionalized benzo-15-crown-5 (B15C5) (Scheme 1 and 2). In TPE-(B15C5)<sub>4</sub>, the TPE core and four outer B15C5 moieties serve as the AIE-active motif and supramolecular  $K^+$ -recognizing functionalities, respectively. TPE-(B15C5)<sub>4</sub> molecularly dissolves in THF with negligible

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**Scheme 1** Schematic illustration of the construction of a “light-up” fluorometric K<sup>+</sup> probe based on aggregation-induced emission (AIE) of crown ether-functionalized tetraphenylethene, TPE-(B15C5)<sub>4</sub>, induced by supramolecular recognition between K<sup>+</sup> ions and crown ether moieties.

fluorescence emission. As we have envisaged, upon K<sup>+</sup> addition, TPE-(B15C5)<sub>4</sub> can be effectively induced to aggregate due to K<sup>+</sup>-mediated cross-linking *via* the formation of K<sup>+</sup>/B15C5 (1/2 molar ratio) molecular recognition complex in a sandwiched manner.<sup>2,6,13</sup> This process is concomitantly accompanied with the turn-on of fluorescence emission *via* the AIE mechanism. Thus, TPE-(B15C5)<sub>4</sub> can serve as highly sensitive and selective fluorometric off-on K<sup>+</sup> probes (see Scheme 1).

## 2. Experimental

### Materials

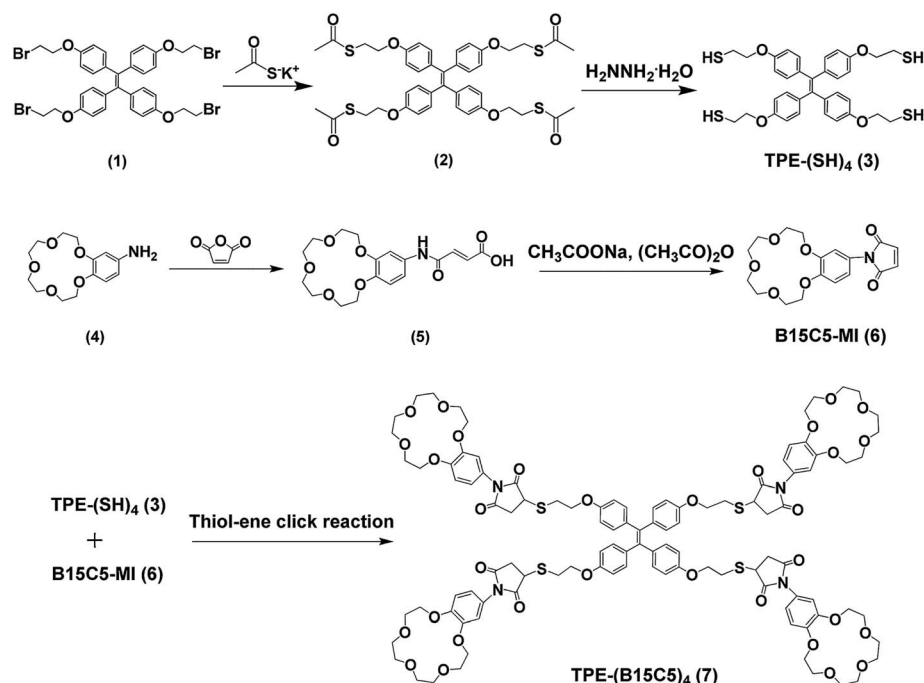
Ethanethioic acid potassium salt (98%), hydrazine hydrate (AR), maleic anhydride (99%), sodium acetate (anhydrous, AR), and

all other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. Thiocyanate salts (K<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Pb<sup>2+</sup>) were dissolved in CH<sub>3</sub>CN as stock solution for all sensing experiments. 1,1,2,2-Tetrakis[4-(2-bromoethoxy)phenyl]ethene (TBEPE, **1**),<sup>14a</sup> and 2,3-(4'-amino-*benzo*-1,4,7,10,13-pentaoxacyclo-pentadeca-2-ene (4'-amino-*benzo*-15-crown-5, **4**)<sup>14b</sup> were synthesized according to literature procedures.

### Sample synthesis

Synthetic schemes employed for the preparation of 1,1,2,2-tetrakis[4-(2-mercaptoethoxy)phenyl]ethane, TPE-(SH)<sub>4</sub>, (**3**), 2,3-(4'-maleimidebenzo)-1,4,7,10,13-pentaoxacyclo-pentadeca-2-ene, B15C5-MI (**6**), and crown ether-functionalized tetraphenylethene, TPE-(B15C5)<sub>4</sub> (**7**), are shown in Scheme 2.

**Synthesis of TPE-(SH)<sub>4</sub> (3).** General protocols for the synthesis of precursor **2** are as follows. TBEPE (2.06 g, 2.5 mmol, 1.0 equiv.) was dissolved in DMF (20 mL). A solution of ethanethioic acid potassium salt (0.428 g, 3.75 mmol, 1.5 equiv.) in DMF (10 mL) was added dropwise over ~20 min. The reaction mixture was stirred at room temperature and the progress was monitored by TLC (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>). After 4 h the reaction was complete and the solvents were removed under reduced pressure. The residues were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed with saturated aqueous NH<sub>4</sub>Cl three times. The organic layer was combined and then washed with HCl (1 M), and saturated brine successively, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to yield a brown solid. Further purification by flash column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) gave (**2**) (1.61 g, 80%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS, Fig. S1†): 6.89 (d, *J* = 8.8 Hz, 8H), 6.62 (d, *J* = 8.8 Hz, 8H), 4.02 (t, *J* = 6.4 Hz, 8H), 3.23 (t, *J* = 6.4 Hz, 8H), 2.35 (s, 12H).



**Scheme 2** Synthetic routes employed for the preparation of crown ether-functionalized tetraphenylethene, TPE-(B15C5)<sub>4</sub> (**7**).

For the synthesis of TPE-(SH)<sub>4</sub>, 0.805 g of **2** (1.0 mmol, 1.0 equiv.) was dissolved in anhydrous THF. Hydrazine monohydrate (250.3 mg, 5 mmol, 5.0 equiv.) in anhydrous THF (10 mL) was added dropwise over ~30 min. The solution was then refluxed overnight. After that, all the solvents were removed under reduced pressure, saturated brine (50 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic phase was washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. Further purification by flash column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) gave **3** as a white solid (318 mg, 50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm, TMS, Fig. S2†): 6.93 (d,  $J$  = 8.7 Hz, 8H), 6.65 (d,  $J$  = 8.8 Hz, 8H), 4.06 (t,  $J$  = 6.4 Hz, 8H), 2.87 (dd,  $J$  = 14.7, 6.4 Hz, 8H).

**Synthesis B15C5-MI (6).** 4'-Aminobenzo-15-crown-5 (**4**, 0.340 g, 1.2 mmol, 1.0 equiv.) was dissolved in 20 mL of anhydrous THF and cooled to 0 °C in an ice-water bath. Maleic anhydride (1.177 g, 12 mmol, 10.0 equiv.) in 10 mL anhydrous THF was added dropwise over 20 min. The reaction mixture was then stirred at room temperature and the progress monitored by TLC. After the reaction was complete, the reaction mixture was evaporated to dryness on a rotary evaporator. The obtained crude product (**5**) was used directly for the next step without any further purification.

Compound **5** obtained in the above step was dissolved in acetic anhydride (25 mL) and heated to 60 °C in an oil bath. Anhydrous sodium acetate (0.246 g, 3.0 mmol) dissolved in anhydrous THF (10 mL) was added. After stirring at 60 °C for 2 h, the reaction mixture was cooled to room temperature and then poured into 80 mL ice-water mixture. The mixture was neutralized with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution and extracted with 3  $\times$  60 mL CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was combined and dried over anhydrous MgSO<sub>4</sub>. CH<sub>2</sub>Cl<sub>2</sub> was then removed on a rotary evaporator and the crude product was further purified by recrystallization from acetone. The final product was dried in a vacuum oven at room temperature overnight to afford a yellow crystal (0.283 g, yield: 65% over two steps). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm, TMS; Fig. S3†): 6.96 (d,  $J$  = 8.4 Hz, 1H), 6.90 (d,  $J$  = 2.2 Hz, 1H), 6.87 (s, 1H), 6.85 (s, 2H), 4.17 (dd,  $J$  = 8.7, 5.5 Hz, 4H), 3.93 (dd,  $J$  = 8.3, 3.7 Hz, 4H), 3.78 (s, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm, TMS, Fig. S4†): 196.6, 148.9, 134.1, 131.2, 119.3, 113.8, 112.4, 70.9, 70.3, 69.3.

**Synthesis of crown ether-functionalized tetraphenylethylene (TPE-(B15C5)<sub>4</sub>, 7).** Compound **6** (100 mg, 0.275 mmol, 8.0 equiv.) was dissolved in anhydrous DMF (10 mL) and degassed by bubbling with N<sub>2</sub> for 30 min. Compound **3** (22 mg, 0.034 mmol, 1.0 equiv.) was then added. After being thermostated at 35 °C in an oil bath and stirred for two days, the resulting mixture was evaporated to dryness on a rotary evaporator and then dissolved in a minimal amount of boiling THF. By cooling the THF solution to -20 °C for several hours, the target product, TPE-(B15C5)<sub>4</sub>, crystallizes from cold THF. After centrifugation and drying in a vacuum oven overnight at room temperature, a white powder was obtained (48 mg, yield: 68%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm, TMS; Fig. S5†): 6.60–7.20 (Ar-*H*, 28H); 4.00–4.12 (*H*<sub>c</sub>' and *H*<sub>j</sub>', 24H); 3.77 (24H, *H*<sub>j</sub>' and *H*<sub>d</sub>'); 3.60 (*H*<sub>k</sub>'). ESI-MS (*m/z*; Fig. S6†): calcd. for [M + 2Na]<sup>2+</sup>, 1067.328; found, 1067.33.

**Fluorometric sensing of K<sup>+</sup> ions.** Fluorescence spectra were recorded using a RF-5301/PC (Shimadzu) spectrofluorometer. The temperature of the water-jacketed cell holder was controlled by a programmable circulation bath. The slit widths were set at 5 nm for both excitation and emission. The fluorescence experiments were conducted using 4.8  $\mu$ M of **7** in THF solution. The effect of the various cations on the fluorescence emission intensity was examined by adding 2.0  $\mu$ L CH<sub>3</sub>CN stock solution of thiocyanate salts into 2.0 mL THF solution of compound **7** (4.8  $\mu$ M) so that the volume increase upon addition of cations can be neglected.

### Characterization

All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV300 NMR spectrometer (resonance frequency of 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C) operated in the Fourier transform mode. ESI-MS experiment was performed on Agilent 6460 Triple Quadrupole mass spectrometer equipped with an ESI source, and exact masses were measured using a Thermo Scientific LTQ Orbitrap Mass Spectrometer equipped with an electrospray interface. UV-Vis absorption spectra were acquired on a TU-1910 double-beam UV-Vis spectrophotometer (Puxi, General Instrumental Company, China). Atomic force microscopy (AFM) measurements were performed on a Digital Instrument Multimode Nanoscope IIID operating in the tapping mode under ambient conditions. Silicon cantilever (RFESP) with resonance frequency of ~80 kHz and spring constant of ~3 N m<sup>-1</sup> was used. The set-point amplitude ratio was maintained at 0.7 to minimize sample deformation induced by the tip. The sample was prepared by dip coating the mixture of TPE-(B15C5)<sub>4</sub> (4.8  $\mu$ M) and K<sup>+</sup> ions (19.2  $\mu$ M, 1.0 equiv.) in THF onto freshly cleaved mica surfaces. Dynamic light scattering (DLS) experiments were conducted on a Malvern Zetasizer Nano ZS Instrument.

### 3. Results and discussion

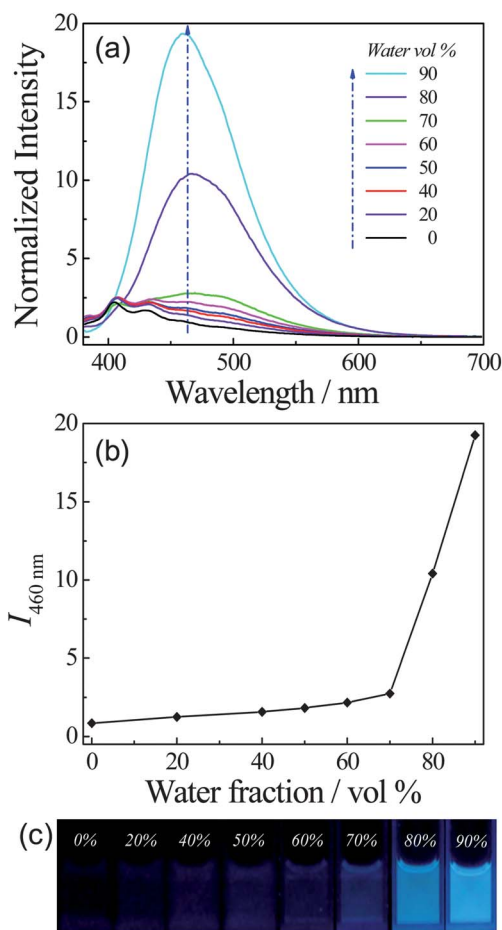
Crown ether-functionalized tetraphenylethylene, TPE-(B15C5)<sub>4</sub> (**7**), was prepared following synthetic routes shown in Scheme 2. Thiolated TPE, TPE-(SH)<sub>4</sub> (**3**) was synthesized at first *via* the reaction of 1,1,2,2-tetrakis[4-(2-bromoethoxy)phenyl]ethene (TBEPE, **1**) with ethanethioic acid potassium salt followed by hydrazinolysis with hydrazine hydrate. The chemical structures of precursor **2** and TPE-(SH)<sub>4</sub> (**3**) were characterized by <sup>1</sup>H NMR (Fig. S1 and S2†). The synthesis of maleimide-functionalized benzo-15-crown-5 (B15C5-MI, **6**) proceeded *via* the reaction of 4'-aminobenzo-15-crown-5 (**4**) with maleic anhydride followed by treatment with acetic anhydride. The chemical structure of **6** was also confirmed by <sup>1</sup>H NMR (Fig. S3†) and <sup>13</sup>C NMR (Fig. S4†) characterization. Taking advantage of the highly efficient thiol-ene click reaction between TPE-(SH)<sub>4</sub> (**3**) and B15C5-MI (**6**), TPE derivatives containing four B15C5 moieties at the periphery, TPE-(B15C5)<sub>4</sub> (**7**) was successfully obtained. A comparison of the <sup>1</sup>H NMR spectrum of **7** with those of **3** and **6** further confirmed the successful synthesis of **7**. Note that considerable peak broadening in the <sup>1</sup>H NMR spectrum of **7** was observed and this can be ascribed to the slow relaxation of **7** due to its high molecular weight (~2089 Da). In the <sup>1</sup>H NMR

spectrum of **7**, the resonance signal ascribing to TPE- $\text{OCH}_2\text{CH}_2\text{S}$  ( $H_c'$ , 4.10 ppm) still remains, whereas the resonance signal at 2.87 ppm in the spectrum of **3** ( $H_d$ ) ascribing to TPE- $\text{OCH}_2\text{CH}_2\text{SH}$  completely disappeared, which shifted to 3.77 ppm ( $H_d'$ ) in the NMR spectrum of **7**. In addition, peak integral ratios between resonance signals characteristic of aryl protons (6.6–7.2 ppm) and those *aryl*- $\text{OCH}_2$  (28 : 24) further confirmed the chemical structure of **7** (Fig. S5†). Furthermore, ESI-MS characterization results of TPE-(B15C5)<sub>4</sub> (**7**) is shown in Fig. S6† ( $m/z$ : calcd. for  $[\text{M} + 2\text{Na}]^{2+}$ , 1067.328; found, 1067.33) and can further confirm its chemical structure. The detection of **7** in the dicationic form can be evidenced by intervals of the observed isotope distributions (*ca.* 0.5). The above results clearly supported that all four thiol moieties of TPE-(SH)<sub>4</sub> (**3**) have participated in the Michael addition reaction and that TPE-(B15C5)<sub>4</sub> (**7**) was successfully synthesized.

In order to check whether the as-synthesized TPE-(B15C5)<sub>4</sub> (**7**) was endowed with the same AIE characteristics as those exhibited by TPE,<sup>7,9,10</sup> we investigated the fluorescence emission of **7** in THF/water mixtures at varying water fractions. When excited at 360 nm, the THF solution of TPE-(B15C5)<sub>4</sub> exhibited quite weak fluorescence emission (Fig. 1), indicating that **7** is non-emissive when at a molecularly dissolved state. In contrast, when water was added into the THF solution, the fluorescence emission increased gradually, and a dramatic emission enhancement was observed when the water fraction is higher than 70 v/v%. Thus, we confirmed that the emission behavior of TPE-(B15C5)<sub>4</sub> is quite comparable to those of TPE and its fluorescence emission can be off-on switched *via* the AIE effect due to aggregates formation at higher water fractions.

Considering the AIE feature of TPE core and the supramolecular recognition between  $\text{K}^+$  ions and peripheral crown ether moieties,<sup>2,6,13</sup> we envisage that the addition of  $\text{K}^+$  will induce the aggregation of **7** and turn on the fluorescence emission, through which, the fluorometric detection of  $\text{K}^+$  can be achieved. As shown in Fig. 2, upon gradual addition of  $\text{K}^+$  ions into the THF solution of **7** (4.8  $\mu\text{M}$ , [B15C5] = 19.2  $\mu\text{M}$ ), the fluorescence emission intensity at 460 nm increased considerably. At  $[\text{K}^+] = 9.6 \mu\text{M}$  (corresponding to  $[\text{K}^+]/[\text{B15C5}] = 1/2$ ), the solution of **7** was getting strongly emissive, with the emission intensity being  $\sim 7.5$ -fold higher than that in the absence of  $\text{K}^+$  ions; at  $[\text{K}^+] = 19.2 \mu\text{M}$  (corresponding to  $[\text{K}^+]/[\text{B15C5}] = 1/1$ ), the emission intensity of the solution reached a value that is  $\sim 9.5$ -fold higher than the blank control. Furthermore, the enhancement of fluorescence emission induced by the presence of  $\text{K}^+$  ions can also be readily discerned by the naked eye (Fig. 2c). If we arbitrarily define the detection limit of  $\text{K}^+$  ions as the concentration at which 10% emission enhancement can be achieved by employing 4.8  $\mu\text{M}$  of **7** in THF solution, the detection limit was then determined to be  $\sim 1.0 \mu\text{M}$ .

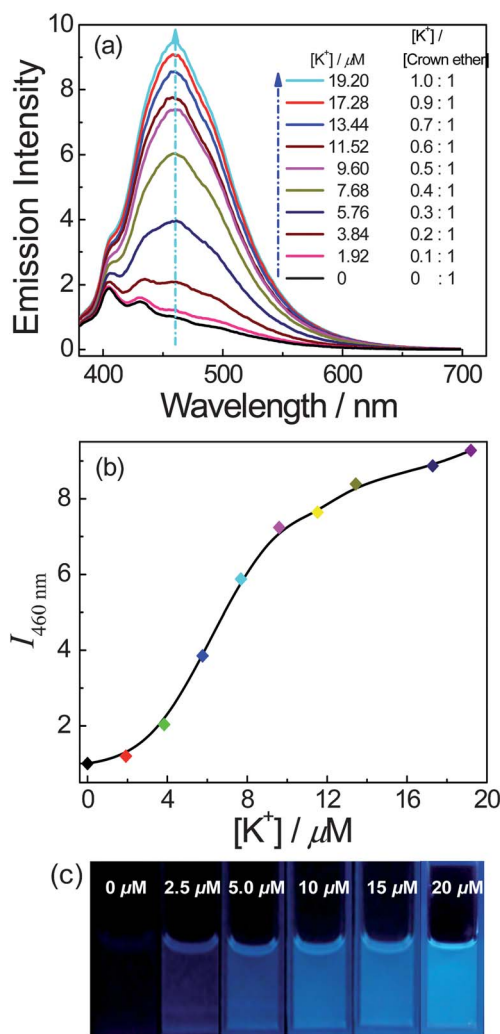
The fluorescence emission enhancement behavior observed for **7** in THF in the presence of  $\text{K}^+$  ions can be attributed to the supramolecular recognition between peripheral crown ether moieties of **7** and  $\text{K}^+$  ions, which leads to the formation of  $\text{K}^+/\text{B15C5}$  sandwich complex in a 1 : 2 molar ratio and the concomitant formation of cross-linked network with TPE-(B15C5)<sub>4</sub> (**7**) as the building block (see Scheme 1). The network formation leads to the turn-on of RIR process, simultaneously boosting the fluorescence emission of TPE cores, this mechanism



**Fig. 1** (a) Fluorescence emission spectra ( $\lambda_{\text{ex}} = 360 \text{ nm}$ ; slit widths: Ex. 5 nm, Em. 5 nm;  $25^\circ\text{C}$ ), (b) normalized fluorescence intensity changes at  $\lambda_{\text{em}} = 460 \text{ nm}$ , and (c) optical photographs recorded under 365 nm UV irradiation for TPE-(B15C5)<sub>4</sub> (4.8  $\mu\text{M}$ ) in THF/H<sub>2</sub>O mixtures with the volume fractions of water varying in the range of 0–90%.

has previously proposed by Tang and coworkers.<sup>7,9,10</sup> It is worthy of noting that before the introduction of AIE concept in 2001 by Tang *et al.*,<sup>7</sup> Li *et al.*<sup>11,16</sup> reported an example of crown ether-functionalized styryl chromophore, which also exhibits the AIE-like fluorometric emitting properties in the presence of  $\text{K}^+$  ions or  $\text{Cs}^+$  ions due to supramolecular recognition between alkaline metal ions and crown ether moieties. Li *et al.*<sup>11</sup> termed the system as “self-assembling fluorescence enhancement”.

We also found the choice of solvents also plays key roles in observing the  $\text{K}^+$ -induced AIE. In preliminary experiments, we have also tried  $\text{CHCl}_3$ , DMSO, and acetone as the solvents. However, for **7** dissolved in  $\text{CHCl}_3$ , the addition of  $\text{K}^+$  typically leads to the formation of quite large aggregates, which prevents the continuous monitoring of  $\text{K}^+$  concentration-dependent emission enhancement. This might be ascribed to the fact that in  $\text{CHCl}_3$ , the molecular recognition events between B15C5 moieties and  $\text{K}^+$  is more favored compared to that in THF.<sup>2,6,13</sup> When using DMSO as the solvent, the  $\text{K}^+$ -induced emission enhancement was not that prominent as compared to those in THF or  $\text{CHCl}_3$ . In acetone and acetonitrile, negligible fluorescence turn-on can be observed. Thus, it turned out that THF is the best choice in terms of the compromise between emission turn-on



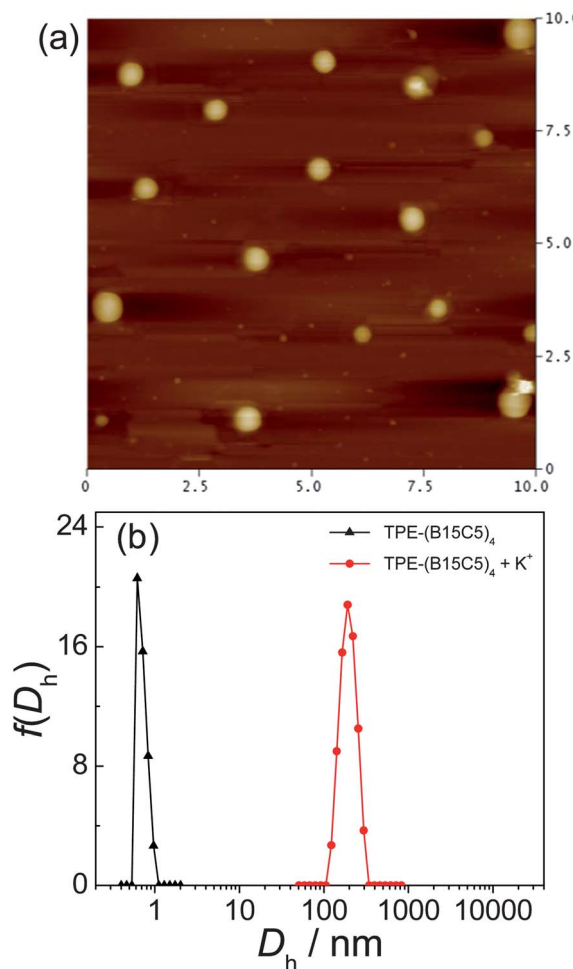
**Fig. 2** (a) Fluorescence emission spectra ( $\lambda_{\text{ex}} = 360$  nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C), (b) relative emission intensity changes at  $\lambda_{\text{em}} = 460$  nm, and (c) optical photographs recorded under 365 nm UV light irradiation for TPE-(B15C5)<sub>4</sub> solution in THF upon gradual addition of K<sup>+</sup> ions (0–1.0 equiv. relative to crown ether moieties); TPE-(B15C5)<sub>4</sub> concentrations were fixed to be 4.8  $\mu M$  in all cases.

efficiency and sufficient colloidal stability of the cross-linked network, although the underlying mechanism interpreting the observed phenomenon remains to be solved.

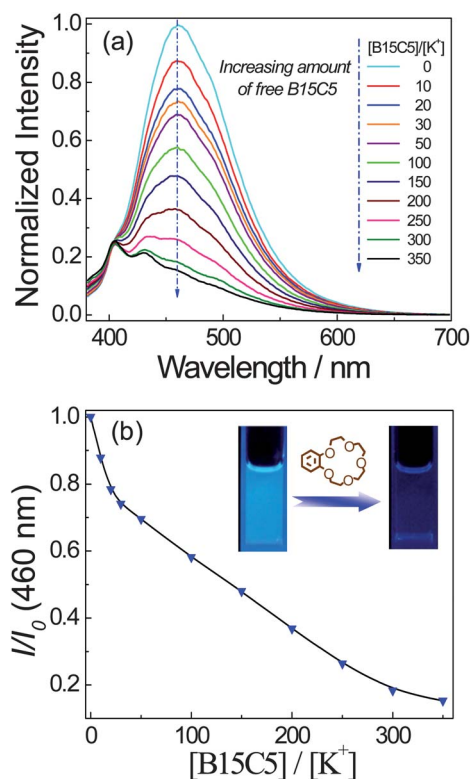
Further experiments were conducted to probe K<sup>+</sup>-induced aggregation of **7** in THF. Fig. S7 shows the UV-Vis absorption spectra of **7** upon addition of varying amount of K<sup>+</sup> ions.<sup>†</sup> The absorption band at around 250 nm decreased and the absorption intensity at around 330 nm gradually increased with the addition of K<sup>+</sup> ions, and an isosbestic point was observed at 290 nm. Furthermore, absorbance baselines at >400 nm also gradually increased, suggesting the formation of colloidal aggregates. Furthermore, AFM measurements for the **7**/K<sup>+</sup> mixture in THF directly revealed the formation of supramolecular cross-linked spherical nanoparticles with the average dimension being ~230 nm (Fig. 3a and Fig. S8<sup>†</sup>). Also note that the nanoparticles are quite monodisperse in terms of size distributions. The DLS results are shown in Fig. 3b, the intensity-average hydrodynamic

diameter,  $\langle D_h \rangle$ , of **7** in THF is ~1 nm, which indicated that **7** can be molecularly dissolved in THF. However, nanoparticle aggregates of ~200 nm clearly formed upon addition of 1.0 equiv. K<sup>+</sup> ions.

With an attempt to further demonstrate that K<sup>+</sup>-induced aggregation and the emission turn-on *via* AIE was caused by the formation of intermolecular K<sup>+</sup>/crown ether sandwich complexes, further competition experiments were then conducted. As shown in Fig. 4, upon gradual addition of free benzo-15-crown-5 (B15C5) to the mixture of **7** (4.8  $\mu M$ ) and K<sup>+</sup> ions (19.2  $\mu M$ ) in THF, the fluorescence emission intensity at 460 nm gradually decreased. In the presence of a large excess of free B15C5 (~350 equiv. relative to K<sup>+</sup>), the emission spectrum almost restored to resemble that of **7** in the absence of K<sup>+</sup> ions. The inset in Fig. 4b shows that the intense cyan emission of **7**/K<sup>+</sup> mixture was greatly weakened upon addition of free B15C5. The above results confirmed that the supramolecular recognition between **7** and K<sup>+</sup> ions is responsible for K<sup>+</sup>-induced aggregation and emission enhancement.



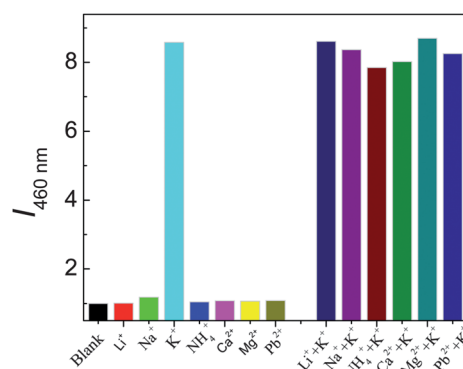
**Fig. 3** (a) AFM height image (10 × 10  $\mu m$ ) recorded for supramolecularly cross-linked nanoparticles formed in the mixture of TPE-(B15C5)<sub>4</sub> (4.8  $\mu M$ ) and K<sup>+</sup> ions (19.2  $\mu M$ ) in THF, (b) DLS profiles of 4.8  $\mu M$  of **7** in THF solution in the absence and presence of 1.0 equiv. K<sup>+</sup> ions, respectively.



**Fig. 4** (a) Normalized fluorescence emission spectra ( $\lambda_{\text{ex}} = 360$  nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C) and (b) emission intensity changes at  $\lambda_{\text{em}} = 460$  nm recorded for TPE-(B15C5)<sub>4</sub> (4.8  $\mu\text{M}$ ) in THF in the presence of 1.0 equiv. of  $\text{K}^+$  ions (relative to crown ether moieties in TPE-(B15C5)<sub>4</sub>) upon gradual addition of free benzo-15-crown-5 (B15C5, 0–350 equiv. relative to  $\text{K}^+$  ions). The inset in (b) shows optical photographs recorded under 365 nm UV irradiation for TPE-(B15C5)<sub>4</sub>/ $\text{K}^+$  mixture in THF before and after the addition of 350 equiv. B15C5.

It is well known that crown ether hosts exhibit strong binding affinity for guest molecules due to their macrocyclic structure and the multidentate binding cooperativity. The binding selectivity largely depends on the host cavity sizes. For B15C5- $\text{K}^+$  host–guest recognition system, the formation of 2 : 1 sandwich complex is thermodynamically favored. Fig. S9 shows Job plot of crown ether moieties in TPE-(B15C5)<sub>4</sub> with  $\text{K}^+$  ions.<sup>†</sup> The total concentration of the hosts (crown ether moieties in TPE-(B15C5)<sub>4</sub>) and guests ( $\text{K}^+$  ions) in THF was fixed at 28.8  $\mu\text{M}$ , and the molar fraction of  $\text{K}^+$  was varied. It is clearly evident that when the molar ratio between  $\text{K}^+$  and crown ether moieties is at 1 : 2, the fluorescence intensity ( $I - I_0$ ) reaches the maximum value (Fig. S9<sup>†</sup>). This demonstrates that crown ether moieties in TPE-(B15C5)<sub>4</sub> form a 2 : 1 stoichiometric complex with  $\text{K}^+$  ions.

Finally, we checked the fluorometric  $\text{K}^+$ -sensing selectivity of **7** in THF over other common cations. As shown in Fig. 5, after addition of 1.0 equiv. of competitive ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Pb}^{2+}$ ), the fluorescence emission of **7** exhibited negligible changes at around 460 nm; however, when 1.0 equiv. of  $\text{K}^+$  ions was added, the fluorescence emission intensity was greatly enhanced either in the presence or absence of competitive ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Pb}^{2+}$ ). These results clearly indicated that **7** can act as a highly selective fluorometric  $\text{K}^+$  chemosensor.



**Fig. 5** Relative emission intensity at  $\lambda_{\text{em}} = 460$  nm recorded for TPE-(B15C5)<sub>4</sub> (4.8  $\mu\text{M}$ ) in THF solution upon addition of 1.0 equiv. different interfering ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Pb}^{2+}$ ) and upon addition of 1.0 equiv.  $\text{K}^+$  ions in the absence or presence of 1.0 equiv. different interfering ions, ( $\lambda_{\text{ex}} = 360$  nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C).

## 4. Conclusions

In summary, a novel “light up” fluorometric  $\text{K}^+$  probe based on the AIE feature of crown ether-functionalized tetraphenylethene, TPE-(B15C5)<sub>4</sub> (**7**), was successfully constructed. The fluorometric  $\text{K}^+$  detection limit can be down to  $\sim 1.0$   $\mu\text{M}$  and it also exhibits excellent selectivity over other common cations such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Pb}^{2+}$ . It works on the basis of  $\text{K}^+$ -induced aggregation of **7** in THF via the formation of supramolecular  $\text{K}^+$ /crown ether 1 : 2 sandwich complex. In addition, quite uniform spherical supramolecular nanoparticles possessing internally cross-linked networks formed in solution. Further experiments are currently underway to demonstrate the practical application of the reported AIE-based fluorometric  $\text{K}^+$  sensing system, for example, the design of novel analogues of **7** with good water solubility for the *in situ* detection and imaging of  $\text{K}^+$  ions under physiological conditions.

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