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Rational Design of A Fluorescent Poly(*N*-aryleneindole ether sulfone) Switch by Cation–π Interactions

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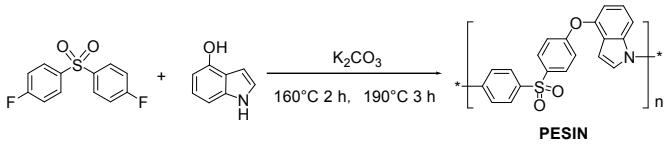
Semirigid poly(*N*-aryleneindole ether sulfone) (PESIN) as a fluorescence emission on-off switch has been successfully achieved via the cation–π interactions. The adjustment of the protonation/deprotonation status of pyridine that regulates the formation of cation–π interactions is definitely the determinant.

In supramolecular chemistry, the noncovalent binding interactions including H-bondings, stacking interactions, cation–π interactions as well as hydrophobic interactions etc. are the basis of a great deal of processes. In recent years, cation–π interactions have received considerable theoretical[1,2] and experimental[1,3] attention, owing to the pivotal roles they play in multidisciplinary areas of research[1,3-4] such as biology, organic synthesis and the design of host-guest assemblies. The interaction between an electron-rich π system (e.g., benzene and indole) and adjacent cations (e.g., Na^+ and K^+) or species containing positive charges (e.g., quaternary ammonium) has been experimentally verified.[1,3] Yamada and coworkers[3a] have shown that a cation–π interaction between a pyridinium ring and an aromatic ring plays a key role in the stereoselective photodimerization of trans-styrylpyridines in a HCl-methanol solution. Other notable examples reported by Lee and coworkers on reduced graphene oxide nanosheets,[3d] and Hwang et al. on the nanomechanics of cation–π interactions in aqueous solution,[3e] further demonstrated the importance of electron-rich aromatics and their binding to cations. Nonetheless, there is no report up to now for fluorescent switches based on either small molecules or polymers via cation–π interactions.[1] Thus, designing new fluorescence emission on-off switches by cation–π interactions is important for fundamental understanding as well as developing new methods for detecting analytes.

To date, polymer as chemosensors allowing for the effective detection of analytes constitute a major current focus in green chemistry.[5-10] New analytical tools are needed for real-time industrial process monitoring and for preventing the formation of toxic materials. Recently, polymer fluorescent switches have attracted extensive interest to analytical scientists.[5,6b] Therefore, it is reasonable to expect that the photo-switchable recognition of polymers is an appealing approach for applications in many related environmental or biological fields.

In the past decades, polyindole and its derivatives prepared by electrochemical oxidation of indole or chemical oxidation using $FeCl_3$ or $CuCl_2$ have received significant attention in many areas such as rechargeable batteries, diodes, and light-emitting diodes (LEDs).[11-14] However, these polymers containing rigid backbone as a result of wholly aromatic or heteroaromatic repeating units are usually poor solubility toward common organic solvents.[14c] To the best of our knowledge, there are only a few reports regarding the utilization of polyindoles as polymer sensors.[15] Hence, the creation of fluorescence emission on-off switches based on polyindoles continues to be a challenging and fascinating task. Lately, we have synthesized a series of soluble poly(*N*-aryleneindole ether)s (PEINs) with promising photoluminescence,[16] owing to the existence of a "push-pull" π-electron mode in the main chain, in which the indole segment served as the electron donor and the electron-deficient group like sulfone functioned as the electron acceptor. Moreover, we also found that the introduction of flexible linkages such as ether or sulfone groups into the polyindole main chain could

enhance their poor solubility. Considering the indole ring as an electron-rich π system and the findings mentioned above, in this paper, we wish to establish a novel polymer receptor of ether-linked poly(*N*-aryleneindole ether sulfone) (**PESIN**) as a fluorescent switch to recognize the aromatic *N*-heterocyclic cations by making full use of cation–π interactions, since these noncovalent interactions could interrupt the "push-pull" π-electron mode, leading to the change of the polymer's fluorescence. Herein, we surprisingly found that the polyindole ether sulfone has an obvious optical responsive property with pyridine hydrochloride (Py·HCl) and its derivative quinoline hydrochloride (Qu·HCl) among the other aromatic *N*-heterocyclic hydrochlorides investigated such as imidazole hydrochloride and benzimidazole hydrochloride in aqueous solutions and shows a visual "turn off" fluorescence. Depending on whether the cation–π interactions exist between the pyridinium rings and the aromatic indole rings, interesting fluorescent ON-OFF-ON processes are observed. The uniqueness of this assay is that the polymer fluorescent switch is successfully achieved through mediating the formation of the cation–π interactions in the system. These studies will help us to gain a deeper insight into the influences of cation–π interactions between host and guest on the complexation behaviors in molecular sensing.



Scheme 1 Synthesis of polymer sensor **PESIN**.

The luminescent polymer receptor **PESIN** was prepared from a nucleophilic substitution C-N/C-O coupling polycondensation reaction of 4-hydroxyindole monomer with activated 4,4'-difluorodiphenyl sulfone in *N*-methylpyrrolidinone (NMP) (Scheme 1). This method of polymerization afforded well-defined polymer in high yield (up to 96%). The molecular weight was determined by gel permeation chromatography (GPC) on a Wyatt DAWN HELEOS with *N*,*N*-dimethylformamide (DMF) as the eluent and relative to polystyrene standards. GPC analysis showed the high molecular weight corresponding to approximately a 438 repeating unit (M_w = 486000, M_n = 152100, polydispersity index (PDI) = 3.20). Detailed experimental procedures and characterization data, including the NMR and IR spectra, are provided in the Electronic Supplementary Information (ESI†).

As expected, the indole-containing polymer (1.0×10^{-5} M corresponding to the indole moiety in DMF) strongly absorbed in the UV and displayed strong luminescence (Fig. 1). The receptor was shown in two strong absorption peaks centered at 266 and 321 nm and exhibited a fluorescence emission at 458 nm. The fluorescence quantum yield (Φ_F) determined in DMF solution using quinine sulfate (Φ_F = 0.55 in 1 M H_2SO_4) as standard was 49.0%.[17] Based on literature precedent, **PESIN** is thought to easily bind with cations by cation–π interactions.[3e] In addition, due to the presence of a "push-pull" π-electron mode in the main chain, when the guest is in binding with the sensor through the cation–π interactions, the distribution of the electron densities of the luminophores could be changed to give rise to the variations of optical signal. Accordingly, it is anticipated that the fluorescence emission of the polymer would be altered upon interaction with species containing positive charges. Pyridine and its analogue derivatives are interesting targets for molecular recognition studies due to their pronounced biological activity.[18] For this purpose, we herein screened a variety of aromatic *N*-heterocyclic cations as potential guest for the polymer receptor **PESIN** and found that this polymer would serve as a fluorescent switch to signal pyridinium and its analogue derivative quinolinium selectively in aqueous solutions.

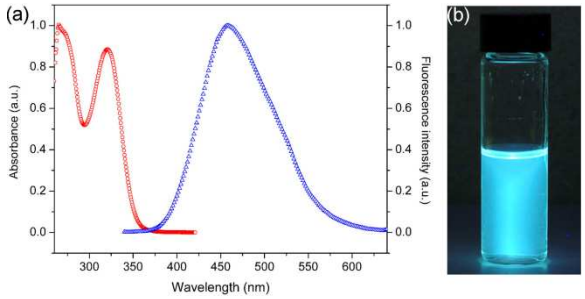


Fig. 1 (a) UV and Fluorescence spectra of **PESIN** in DMF solution. Solution concentration: 10 μM; excitation wavelength: 320 nm; excitation and emission slits (nm): 10.0 nm and 2.5 nm, respectively. (b) Fluorescence images of **PESIN** in DMF (λ_{ex} = 365 nm).

The binding capabilities of polymer receptor **PESIN** were first conducted by measuring the fluorescence variation of **PESIN** (10 μM) upon addition of a variety of aromatic *N*-heterocyclic hydrochlorides including pyridine hydrochloride (Py·HCl), quinoline hydrochloride (Qu·HCl), imidazole hydrochloride (IM·HCl) and benzimidazole hydrochloride (BIM·HCl) in 99:1 (v/v) of DMF/H_2O. Fig. 2a clearly shows that Py·HCl and Qu·HCl both caused >61% fluorescence quenching at 458 nm. Other *N*-heterocyclic hydrochlorides, such as IM·HCl and BIM·HCl induced much smaller or negligible changes. The experimental results demonstrated that polymer receptor **PESIN** had more obvious recognition ability towards Py·HCl and Qu·HCl over the other aromatic *N*-heterocyclic hydrochlorides examined. We speculated that the preorganization of the receptive sites of the host sufficiently utilized the supramolecular interactions only with structurally complementary guest molecules. Hence, receptor **PESIN** with flexibility could adopt a predominant configuration to bind the guest molecule such as Py·HCl or Qu·HCl, and these subtle interactions led to the formation of a relatively stable complex between **PESIN** and the guest.

Subsequently, fluorescence titration experiments of **PESIN** towards Py·HCl and Qu·HCl were carried out. As shown in Fig. 2b, taking Py·HCl as a representative example, the fluorescence intensity of **PESIN** at λ_{em} = 458 nm decreased constantly with an increase in the pyridine hydrochloride

concentration. In addition, the fluorescent quenching effect (%) amounted to ca. 93% without shift in wavelength when 3 mM of Py·HCl were added into the solution of **PESIN**, indicating that no excimer was formed. The receptor **PESIN** showed chelation enhanced quenching (CHEQ) effect with Py·HCl, implying that the interuption of the intramolecular charge transfer. According to the nonlinear curve fitting,[19] the measured emission [F] at 458 nm varied as a function of Py·HCl in a linear relationship (R>0.999), indicating that the repeating unit of **PESIN** and Py·HCl could form a 1:1 complex. The association constant of **PESIN** with Py·HCl was calculated as $(5.57 \pm 0.21)\times10^2$ M^{-1} (Fig. S1†). While the calculated association constant is significantly higher than that of a copper(II) metal complex for pyridine $(0.94 \pm 0.07)\times10^2$ M^{-1}.[18a] The binding interaction of **PESIN** with Qu·HCl also formed the 1:1 complex with a higher association constant than that of **PESIN** with Py·HCl under the identical conditions ($(6.89 \pm 0.34)\times10^2$ M^{-1}, Fig. S2†). Detection limits were estimated (based on the criteria of fluorescence quenching) from the titration results, and have values of 7.0×10^{-5} M and 5.1×10^{-5} M for Py·HCl and Qu·HCl, respectively.[20] As a result, it is clear that the most striking effect was observed for Qu·HCl.

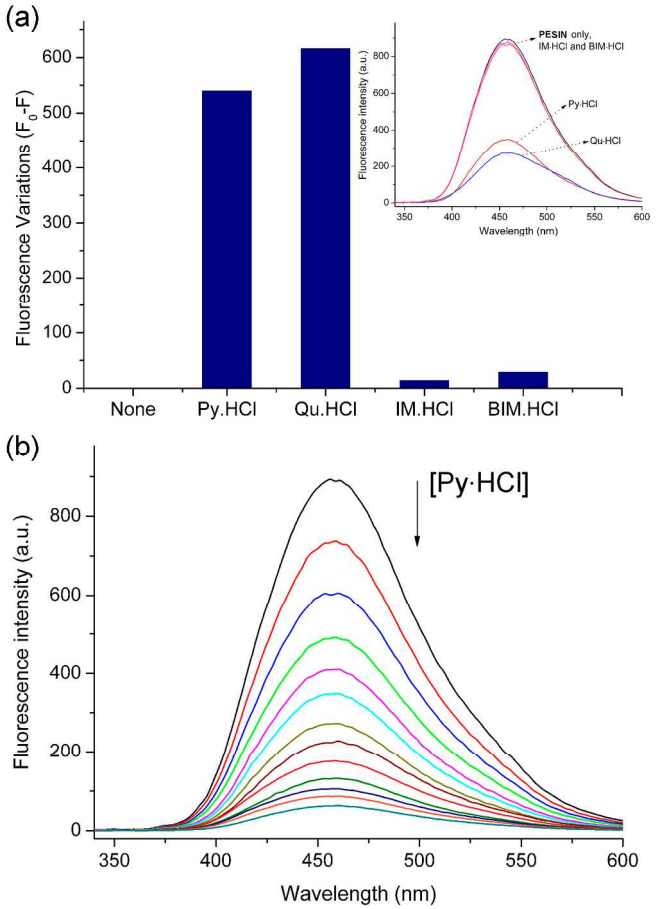


Fig. 2 (a) Fluorescence variations and fluorescence spectra (inset) of **PESIN** (10 μM) upon addition of 125 equiv. of aromatic heterocyclic hydrochlorides in 99:1 (v/v) of DMF/H_2O, excited at 320 nm. F and F_0 are the fluorescence intensity of **PESIN** at 458 nm with and without hydrochlorides, respectively. The aromatic *N*-heterocyclic hydrochlorides are Py·HCl, Qu·HCl, IM·HCl, and BIM·HCl. (b) Fluorescence spectra (λ_{ex} = 320 nm, slits = 5.0 nm, 3.5 nm) of the DMF/H_2O (99:1, v/v) solution of **PESIN** (10 μM) in the presence of Py·HCl (From top to bottom: 0, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300 equiv.) at 25 °C.

To further shed light on the possible origin of the significant performance of **PESIN**, pyridine, hydrochloride and triethylamine hydrochloride (Et_3N·HCl) were next chosen for comparation. It was found that the addition of pyridine or hydrochloride to **PESIN** showed just slight fluorescence quenching in the spectra (Fig. S3†). These observations clearly suggested that the important role of the host-guest interactions (cation–π interactions). More importantly, a negligible change was observed upon the addition of Et_3N·HCl to **PESIN**. On this basis we assumed that many of the cation–π interactions between the main chain groups of zigzag polymer cannot achieve an optimized bond distance because of steric restrictions.[3e,16]

Moreover, ^{1}H NMR experiments in DMSO-d_6 were carried out to look into the effects of pyridine hydrochloride on **PESIN**. Fig. 3 shows the ^{1}H NMR spectra of **PESIN** recorded in the absence and presence of 1.0 equiv. of Py·HCl in DMSO-d_6. Upon the addition of Py·HCl, distinct ^{1}H NMR spectral changes were observed: the aromatic hydrogen signals of pyridinium moiety underwent obvious upfield shifts by 0.14 ppm to 8.80, 0.13 ppm to 8.49, and 0.11 ppm to 7.98, respectively, indicating that the interactions between the host and guest happened through the expected cation–π interactions from the pyridinium ring. Unfortunately, the peaks of **PESIN** were much broader owing to its polymeric nature and could not be observed the corresponding changes. In addition, pyridinium NH chemical shifts of Py·HCl could not appear in the ^{1}H NMR spectra under this condition.

In contrast to what is seen with Py·HCl, the ^{1}H NMR spectra of pyridine were also recorded in the absence and presence of **PESIN** in DMSO-d_6. However, no detectable changes or trace differences were observed probably due to its lack of positive charges (Fig. 3). These results led us to futher propose that the formation of the cation–π interactions between Py·HCl and **PESIN** leading to a quenching of the fluorescence signal at 458 nm.

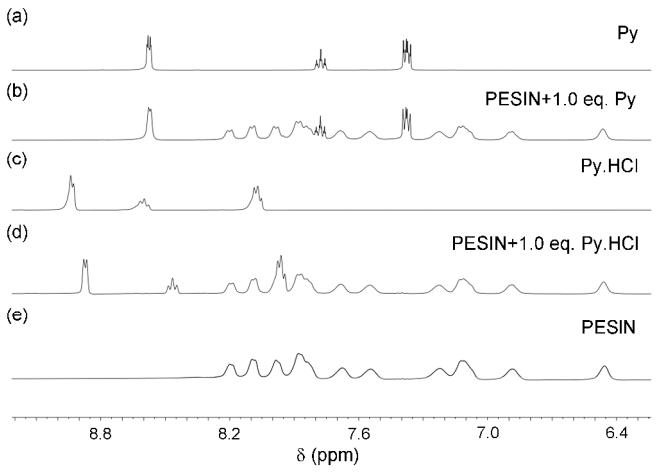


Fig. 3 Partial ^{1}H NMR spectra of **PESIN** and its complex at 25 ºC in DMSO-d_6: (a) pyridine; (b) **PESIN** + 1.0 equiv. of Py; (c) pyridine hydrochloride; (d) **PESIN** + 1.0 equiv. of Py·HCl; (e) **PESIN**.

To confirm the significance of cation–π interactions during the recognition stage, the deprotonation of pyridine hydrochloride in the process of fluorescence titation was conducted followed. **PESIN** was interacted with Py·HCl, and then it was replaced by NaOH. For example, the solution of **PESIN** (10 μM) was treated with Py·HCl (3 mM) to give a quenched solution, followed by the addition of NaOH to deprotonate the acidic $(N–H)^+$ proton, then the fluorescence of receptor **PESIN** was regenerated owing to the disappearance of the cation–π interactions. From Fig. 4, we could see that the fluorescence emission intensity of the solution of **PESIN** and Py·HCl at 458 nm gradually enhanced with an increase in the concentration of NaOH. Such finndings led us to consider that the cation–π interaction between a pyridinium ring and an aromatic indole ring may play a key role in the recognition process. Furthermore, strong fluorescence quenching in the presence of Py·HCl can be applicable to a photoinduced on-off switch.

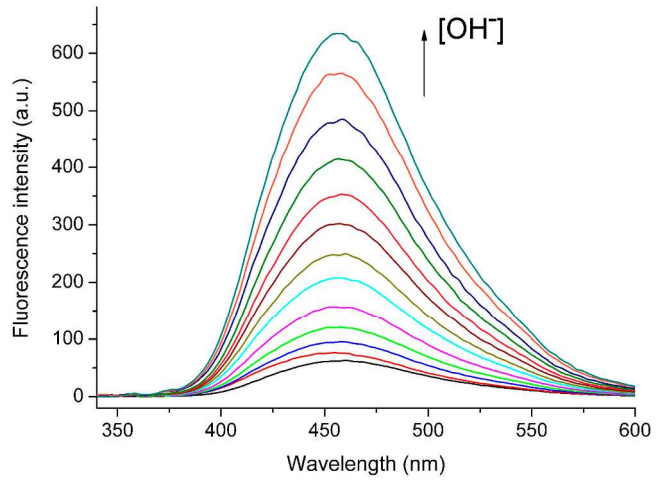


Fig. 4 Fluorescence titration of the quenched solution of **PESIN** (10 μM) and Py·HCl (0.003 M) upon addition of NaOH in 99:1 (v/v) of DMF/H_2O (From bottom to top: 0, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300 equiv.) at 25 °C.

The computational method of molecular dynamics simulation was performed to better understand the mechanism of cation–π interactions between **PESIN** and Py·HCl (Fig. S4†). Generally, the radial distribution function (RDF) is a useful method in the structural investigation of both solid and liquid packing (local structure) for studying specific interactions.[21,22] The resulting function is given by the symbol, $g_{AB}(r)$, and is calculated by averaging over the static relationship of every given pair of atoms, AB, as follows:

$$g_{AB}(r) = \frac{\langle n_{AB}(r) \rangle}{4\pi r^2 \Delta\rho_{AB}}$$

The interaction between the indole moieties of the polymer and the $–N^+H$ groups of the Py·HCl can be investigated by means of the radial distribution function, $g_{AB}(r)$, where A and B are indole groups and $–N^+H$ groups, respectively. $\Delta\rho_{AB}$ is the rate of change of the average number density of $–N^+H$ group with distance from a indole ring. The $g_{AB}(r)$ function gives the local density of B around A at a distance r, and $\langle n_{AB}(r) \rangle$ is the average number of atom pairs between r and r + Δr.

Fig. 5 displays the RDF for the polymer solutions between the nitrogen atoms of the $–N^+H$ groups and the indole rings of the polymer. The peaks of $g_{AB}(r)$ indicated the presence of definite correlations between atoms within that radius, while the absence of any peaks beyond 6Å distance indicated that there was no long-range interaction in the systems. One can consider that cation–π interactions existed if the $–N^+H\cdots$indole distance was in the range of 2~4 Å.[1a,3a,3c] It can be observed that $g_{AB}(r)$ had its largest value (2.08) when the distance between N of the $–N^+H$ groups and indole rings was about 3.21 Å, which indicated that strong cation–π interactions between these groups existed at that distance. The inset in Fig. 5 exhibits the example of the cation–π interactions (ca. 3.566 Å) between $–N^+H$ groups and the indole rings. In the sense of computational chemistry, the expected cation–π interactions would favor the coordination of Py·HCl with the receptor **PESIN**.

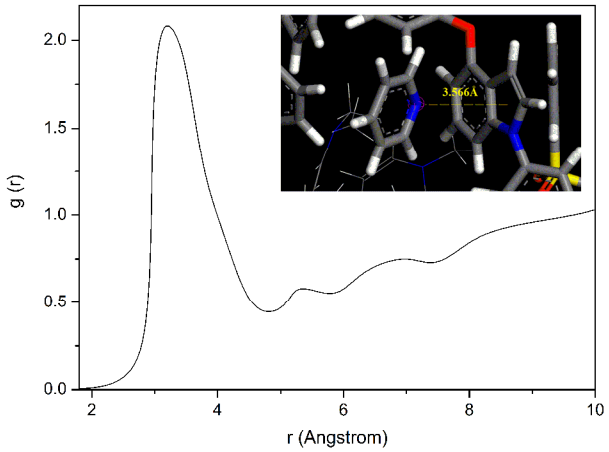


Fig. 5 RDF calculation for nitrogen atoms of the $–N^+H$ groups to the distance of the indole groups. Inset: cation–π interactions between **PESIN** and Py·HCl by simulation.

The counteranion dependence of the recognition experiment was also investigated. As seen in Fig. S5,† almost the identical fluorescence quenching was obtained when 1.25 mM of pyridine hydrochloride (Py·HCl), pyridine hydrobromide (Py·HBr) and pyridine sulfate ($Py·H_2SO_4$) were added into a solution of **PESIN**, respectively. These observations demonstrated that the recognition mechanism may greatly rely on the species containing positive charges such as pyridinium and be independent of the counteranions in the solution.

Based on the above key findings, a plausible mechanism pathway for the formation of complex between **PESIN** and Py·HCl is proposed in Fig. 6. The achieved **PESIN** showed zigzag molecular chain structure and the "push-pull" π-electron mode in the chain made it emit a cyan light (Fig. 6a).[16] When the hydrochloride was added into the solution of **PESIN**, due to

the absence of host-guest interactions like cation–π interactions, these ions including H^+ and Cl^- were dispersed around the polymer sensor randomly. Therefore, negligible changes in the fluorescence intensity were observed (Fig. 6b). As shown in Fig. 6c, an amount of pyridine also caused no or slight fluorescence changes. In contrast, the phenomenon of quenching fluorescence appeared if Py·HCl guest was formed in the solution (Fig. 6d). We concluded that the formation of cation–π interactions between the relatively electron-deficient pyridinium ring and the electron-rich indole ring. As a result, the electron density of both host and guest was altered in the complexation course, which further gave rise to chelation enhanced quenching effect and diminished the fluorescence (Fig. 6d). Receptor **PESIN** displayed a better selectivity recognition of Py·HCl and a visual "turn off" fluorescence. As shown in Fig. 6e, once introducing the basic OH^- anions to the quenched solution, the vanishing fluorescence was regenerated again owing to the deprotonation of pyridine hydrochloride. It was suggested that the OFF-ON response was mainly dominated by breaking the cation–π interactions.

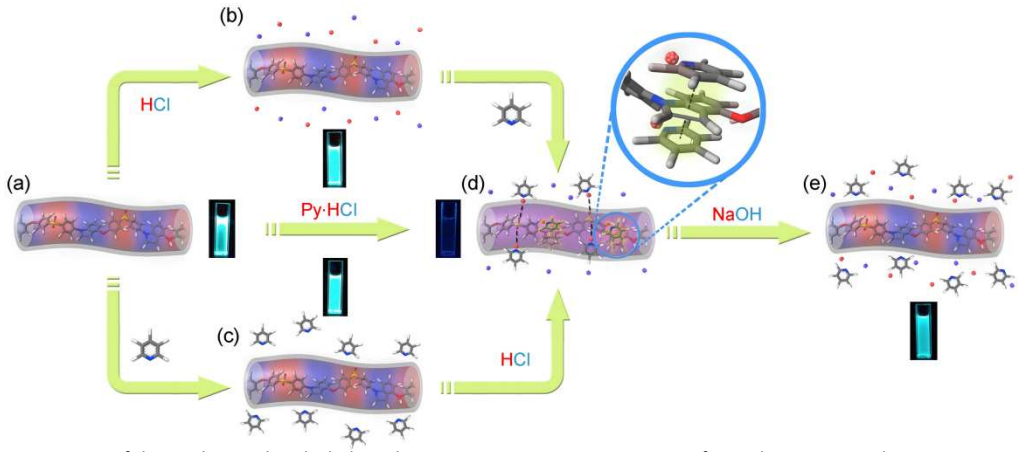


Fig. 6 A schematic representation of the mechanism by which the polymer sensor **PESIN** can recognition of Py·HCl in aqueous solution.

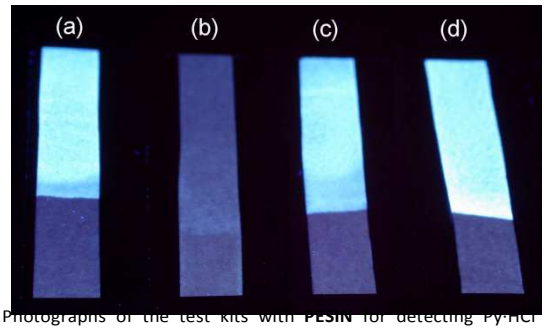


Fig. 7 Photographs of the test kits with **PESIN** for detecting Py·HCl in DMF solution. Left to right: **PESIN**, **PESIN** with Py·HCl, **PESIN** with Py, **PESIN** with Py·HCl and then treated with NaOH.

To investigate the practical application of polymer receptor **PESIN**, test strips were prepared by immersing filter papers into a DMF solution of **PESIN** (0.1 M) and then drying in air. The test strips containing **PESIN** were utilized to sense Py·HCl. The fluorescence quenching caused by Py·HCl was easily discriminated by naked eyes under the common TLC-UV light. As depicted in Fig. 7, to the DMF solutions of Py·HCl (1 M) and pyridine (Py, 1 M), the test kits were immersed for 10 s. For the Py·HCl, the obvious fluorescent quenching change was observed under UV light, λ = 365 nm. On the contrary, such a large amount of Py hardly caused any fluorescence change. More interestingly, the quenched test strip was then immersed into the NaOH solution (1 M) and immediately the fluorescence was regenerated, which was in agreement with the experimental titration results mentioned before. Therefore, the test strips covered with **PESIN** could be recycled and reused for many times. These characteristics make **PESIN** potential candidate for sensing devices of environmental monitoring. In addition, these results lent further support to the inference that the cation–π interaction between the pyridinium ring and the aromatic indole ring was important in the present complexation process.

Conclusions

In summary, we have synthesized a fluorescent poly(*N*-aryleneindole ether sulfone) (**PESIN**) receptor for the recognition of pyridine hydrochloride and its derivative quinoline hydrochloride among the other aromatic heterocyclic hydrochlorides investigated in aqueous solutions via the cation–π interactions. The detection limit of Py·HCl is up to 7.0×10^{-5} M. Through the adjustment of protonation/deprotonation status and electron density of both host and guest on the complexation process, the emission of the system could be turned on-off switch easily. Furthermore, we elucidate the mechanism that results in the ON-OFF-ON fluorescence response, indicating that the existence of the cation–π interaction between the pyridinium ring and the aromatic indole ring in the complexation process plays an important role in the sensing. We believe that these conclusions would be potentially useful for detecting other analytes of interest in biomedical applications via cation–π interactions and might provide a valuable insight into the development of various polymer sensors.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Methods and materials of spectra experiments; additional spectroscopic plots and data; the calculation of the association constants and the detection limits; optimized geometries of polymer solution; IR spectra and copies of ^{1}H NMR. See DOI: 10.1039/c000000x/

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Rational Design of A Fluorescent Poly(*N*-aryleneindole ether sulfone) Switch by Cation–π Interactions

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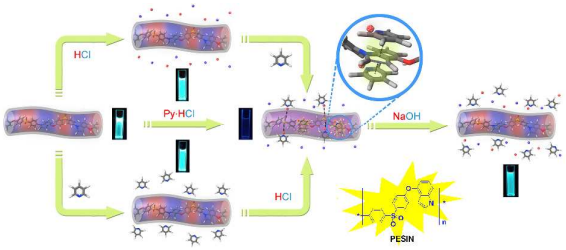

A fluorescence emission on-off switch is achieved by adjusting the assembly of poly(*N*-aryleneindole ether sulfone) (**PESIN**) and pyridine hydrochloride via the cation–π interactions.