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Cite this: *Chem. Commun.*, 2011, **47**, 11014–11016

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Click functionalized poly(*p*-phenylene ethynylene)s as highly selective and sensitive fluorescence turn-on chemosensors for Zn^{2+} and Cd^{2+} ions†

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Received 8th July 2011, Accepted 25th August 2011
DOI: 10.1039/c1cc14113a

Side-chain functionalized poly(*p*-phenylene ethynylene)s (PPEs) carrying triazole linkers, amino donors/receptors, and solubilizing groups have been found to yield remarkably high efficiency of fluorescence turn-on sensing for Zn^{2+} and Cd^{2+} ions in THF, and for H^+ and Cd^{2+} ions in water.

Conjugated polymers (CPs) are chromophores exhibiting significant advantages over other small-molecule based chemosensors in the field of chemical sensory devices.[1] In the current literature, most of the CP fluorescence sensors are designed to use fluorescence quenching (*i.e.* turn-off) as the signal readout mechanism, whereas CP sensors showing fluorescence enhancement (turn-on) sensing behavior are relatively few.[2] Nevertheless, turn-on sensors do have some advantages not so easily attainable by turn-off sensors, including the ease of detecting low concentration contrast relative to a dark background, reduced false-positive signals, and enhanced sensitivity. In this respect, the pursuit of new CP based fluorescence turn-on sensors still remains a topic of considerable interest.

A common design motif for fluorescence turn-on sensors is based on fluorophore-donor ensembles, in which the donor group usually acts as the receptor and binds with analytes to result in fluorescence turn-on based on photoinduced electron transfer (PET) or internal charge-transfer (ICT) mechanisms.[3] This strategy has been successfully applied to the construction of numerous small-molecule sensors.[4] However, it is not trivial for CP fluorophores to achieve good fluorescence turn-on performance due to the high background emission of most CPs as well as the inherent fluorescence quenching effect of some metal ions.[5] Indeed, CP-based fluorescence turn-on sensors for metal ions reported in the literature have only attained weak to moderate fluorescence enhancement (*ca.* 1 to 3-fold).[2c–f] To make further improvement requires new design concepts. For instance, Jones Jr. and co-workers[6] in 2006 devised a tmeda-PPETE sensor preloaded with Cu^{2+} to gain a substantially quenched fluorescence background. Upon displacement with Fe^{2+}, this inorganic/organic hybrid system gave fluorescence enhancement as great as 150-fold.

To our knowledge, solely CP-based chemosensors that exhibit sizable fluorescence turn-on responses to metal ions have not been reported. To address this challenge, we investigated the approach of incorporating amino groups as metal ion receptors into the side chains of poly(phenylene ethynylene)s (PPEs). In our study, the highly emissive nature of PPEs imposed a major obstacle,[7] given that a sufficiently "dark" fluorescence background is a key prerequisite to efficient turn-on sensing. However, a fortuitous discovery we made in an effort of using facile "click" chemistry[8] to generate some functionalized PPEs (*e.g.* **PPE-1** in Fig. 1) offers a satisfactory solution to this problem. In **PPE-1** the 1,2,3-triazole linker resulting from the Cu-catalyzed alkyne azide cycloaddition (click reaction) not only acts as a structural element (linkage) but plays a unique functional role in quenching the fluorescence of PPEs. The effect of triazole on fluorescence

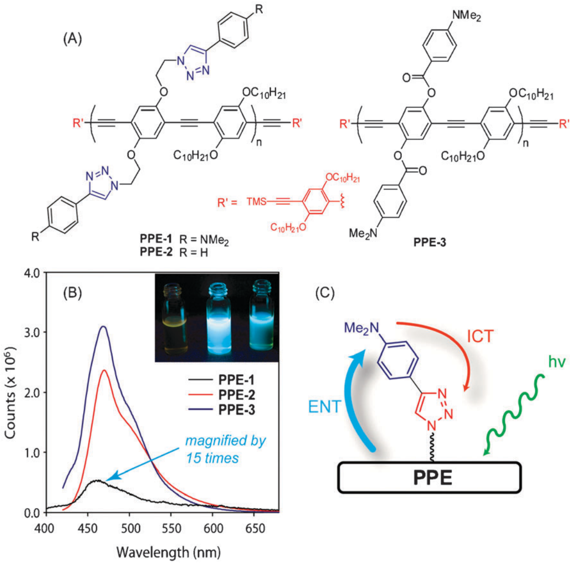

Fig. 1 (A) Molecular structures, and (B) fluorescence spectra of **PPE-1**, **PPE-2**, and **PPE-3**. Spectra were measured in deoxygenated THF at room temperature. Polymer samples were prepared at a concentration of 100 μg/mL. Inset: photographic images of THF solutions of **PPE-1** (left), **PPE-2** (middle), and **PPE-3** (right) under the irradiation of a UV lamp. (C) Proposed fluorescence quenching mechanism for **PPE-1**.

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures of functionalized PPEs and related precursors, as well as spectroscopic characterization data. See DOI: 10.1039/c1cc14113a

quenching is manifested by comparison with two other model PPEs (**PPE-2** and **PPE-3**, Fig. 1).

Of the three polymers, only the fluorescence of **PPE-1** is substantially quenched as clearly evidenced by both visual check (inset of Fig. 1B) and emission quantum yield measurements ($\Phi = 0.038$ for **PPE-1**, $\Phi = 0.74$ for **PPE-2**, and $\Phi = 0.29$ for **PPE-3** in THF). It is also noted that the emission spectral profile of **PPE-1** is markedly different from those of the other two polymers (Fig. 1B). The broad and structureless fluorescence band of **PPE-1** is characteristic of an emissive charge-transfer (CT) excited state.[9] Based on such spectral features, a quenching mechanism is proposed as depicted in Fig. 1C. Upon irradiation, the PPE unit first captures a photon to reach the first excited state (S_1). Rapid energy transfer (ENT) sensitizes the donor (amino) group, triggering an ICT process from the donor (amino) to the acceptor (triazole) group. As such, the fluorescence is quenched by a relay of energy transfer, sensitization, and charge transfer. It should be noted that the combination of aminophenyl-triazole is of indispensible necessity to fluorescence quenching, since high emissivity is retained for the model polymers where only triazole (**PPE-2**) or amino (**PPE-3**) groups are present on the side chains.

With the nearly non-emissive **PPE-1** in hand, its turn-on sensing function towards various metal ions was then tested. THF solutions of **PPE-1** were titrated with various metal ions, ranging from Zn^{2+}, Cu^{2+}, Cd^{2+} to Ba^{2+}, Na^{+}, and Li^{+}. The spectral responses of **PPE-1** were monitored by both UV-Vis absorption and fluorescence spectroscopy (see ESI). In addition to metal ions, **PPE-1** was also subjected to the titration of a strong Brønsted acid, trifluoroacetic acid (TFA). The titration results indicate that **PPE-1** shows prominent fluorescence turn-on responses to certain metal ions in the concentration range of 10^{-6} to 10^{-3} M. Fig. 2A depicts the steady fluorescence enhancement of **PPE-1** upon addition of Zn^{2+} ion. It is worth noting that at the saturation point of titration, the fluorescence of **PPE-1** gains a 51-fold enhancement (at $\lambda_{em} = 462$ nm), which is the greatest among other tested ion species. Besides Zn^{2+}, **PPE-1** also affords a very high sensitivity towards Cd^{2+} ion (*ca.* 34-fold enhancement). Fig. 2B outlines the decreasing trend of sensitivity of **PPE-1** for various cations. Clearly **PPE-1** acts as a highly selective and sensitive chemosensor for Zn^{2+} and Cd^{2+} ions (detection limit: 1×10^{-6} M) in THF.

Apart from THF, sensing properties of click-functionalized PPEs in aqueous media were also explored. It was found that **PPE-1** can be partially solubilized in water/DMSO (1 : 1, v/v) with the aid of surfactants such as sodium dodecylsulfonate (SDS), and the resulting aqueous solution of **PPE-1**/SDS showed selective fluorescence turn-on sensing behavior for Cd^{2+} ion. The sensitivity however was relatively low (< 3-fold enhancement, see Fig. S-8 in ESI), presumably due to the poor solubility and significant aggregation of **PPE-1** in water. To circumvent this problem, a water-soluble polymer analogue, **PPE-4**, was subsequently designed and tested (Fig. 3).

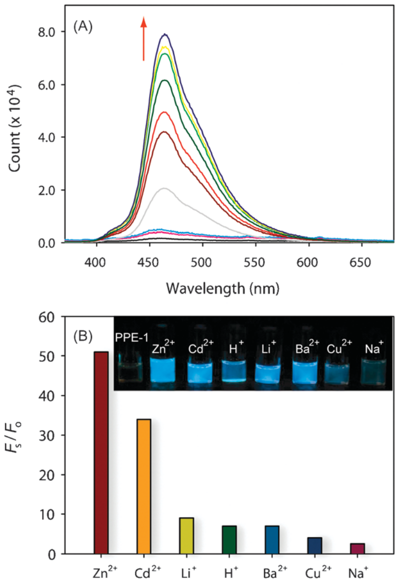

Fig. 2 (A) Fluorescence spectral changes of **PPE-1** (100 μg mL^{-1}, $\lambda_{ex} = 380$ nm) upon titration of $Zn(OTf)_2$ in THF at concentrations of 0.0, 0.0033, 0.010, 0.030, 0.17, 0.83, 1.10, 1.50, 3.45, and 6.20 mM. (B) Trend of fluorescence enhancement (F_s/F_o) for different cations at maximum emission wavelength (F_s: fluorescence intensity at the saturation point of titration; F_o: initial fluorescence intensity). Inset: photographic images of THF solutions of **PPE-1** without and with various cations under the irradiation a UV lamp.

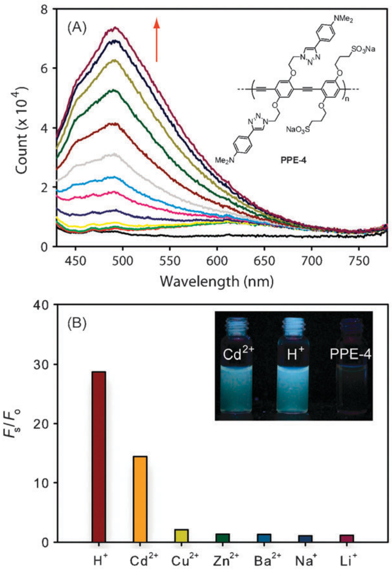

Fig. 3 (A) Fluorescence spectral changes of **PPE-4** (100 μg mL^{-1}, $\lambda_{ex} = 400$ nm) upon titration of $Cd(ClO_4)_2$ in water at concentrations of 0.0, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 6.0, 8.0, 12.0, 20.0, and 28.0 mM. (B) Trend of fluorescence enhancement (F_s/F_o) for different cations at maximum emission wavelength. Inset: photographic images of aqueous solutions of **PPE-4** without and with Cd^{2+} and H^{+} ions.

Fluorescence spectra of **PPE-4** as a function of $[Cd^{2+}]$ in water are shown in Fig. 3A. Analysis of these emission spectral data reveals two distinct steps. At $[Cd^{2+}] \sim 2.0$ to 3.2 mM an emission band at 620 nm grows in, while at $[Cd^{2+}] \sim 2.1$ to 12 mM an intense emission centered at 492 nm grows in. Saturation behavior is observed at $[Cd^{2+}] > 12$ mM. Over the course of titration a 14-fold enhancement of emission intensity is observed (detection limit: 3 mM). The two different stages of spectral changes suggest multiple binding modes are at work in the

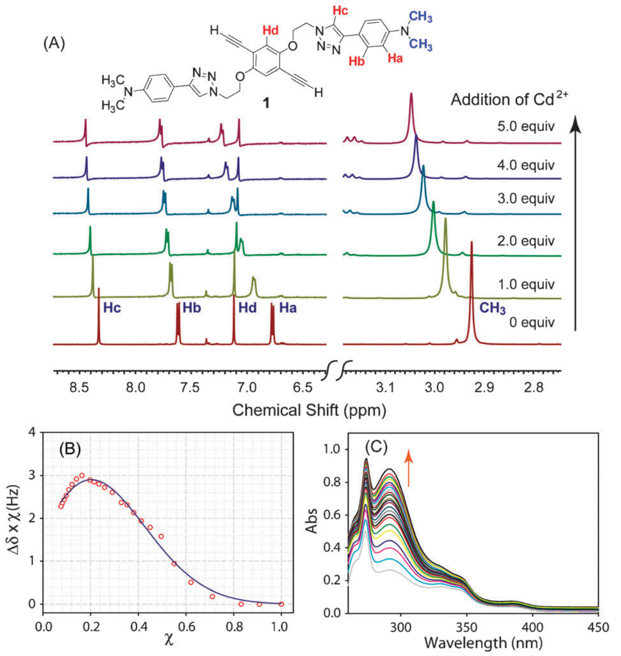

Fig. 4 (A) ^{1}H NMR titration of compound **1** (6.8 mM) with Cd(ClO$_4$)$_2$ in DMSO-*d*$_6$. (B) Job plot of compound **1** in DMSO-*d*$_6$ (Δσ: shift of the CH$_3$ signal; χ: molar fraction). (C) UV-Vis spectroscopic titration of compound **1** (15 μM) in DMSO with Cd^{2+} at concentrations of 0.0, 5.0, 9.9, 15, 20, 24, 29, 34, 38, 43, 48, 52, 57, 65, 74, 83, 91, 110, 130, 170, 200, 260, and 330 mM.

interaction of Cd^{2+} ion with **PPE-4**. Upon titration of **PPE-4** with TFA in water, much stronger fluorescence enhancement (29-fold) and higher sensitivity (detection limit: 0.3 mM) in comparison to Cd^{2+} sensing were observed. The prominent spectral responses to TFA in water indicate that **PPE-4** is more prone to protic acids than metal ions under aqueous conditions. Unlike the two-stage scenario in Cd^{2+} titration, the titration of **PPE-4** with TFA showed only a monotonic emission increase at 492 nm (Fig. S-9, ESI†). The different titration curves suggest that Cd^{2+} might be preferentially bound to the triazole ligand over the amino group at the early stage of titration. In a sharp contrast to **PPE-1**, the sensitivity of **PPE-4** for Zn^{2+} in water was rather diminutive. The statistical graph in Fig. 3B clearly reveals the ability of **PPE-4** to differentiate Cd^{2+} and Zn^{2+} ions in water.

On the side chains of the two PPE sensors, N-containing amino and triazole groups were both expected to act as receptors (ligands) for metal ions. In theory the binding of metal ions to the amino groups should reduce their electron-donating ability. The interaction of Cd^{2+} with either the amino or the triazolyl groups would raise the energy of the ICT state such that excited-state quenching of the PPE backbone becomes endergonic. The proposed mechanism differs from the mechanistic arguments made by Jones Jr. and co-workers.[2c] In the meantime, the binding of triazole with metal ions can also alter non-radiative deactivation steps in the mechanism. In this respect, characterization of the polymer-metal ion interactions is of great value to further unraveling the detailed photophysical mechanisms of the click-functionalized PPE fluorescence turn-on sensors.

To determine the stoichiometry of metal ion binding, monomer **1** (Fig. 4) was prepared as a model compound and its coordination mode with Cd^{2+} ion was examined by ^{1}H NMR and UV-Vis spectroscopy. From Fig. 4A, it can be seen that the NMR signals of the triazolyl and aminophenyl protons (H$_a$, H$_b$, H$_c$, and CH$_3$) of **1** are significantly shifted to the down-field direction upon titration with Cd^{2+} ion. The protons on the central phenyl ring (H$_d$) however show only a slight up-field shift. The results indicate that the amino and triazole groups are both metal ion receptors to effectively interact with Cd^{2+}. This binding mode concurs with the 1 : 4 binding stoichiometry ($\mathbf{1}^{\bullet}$[Cd^{2+}]$_4$) manifested by the Job plot analysis shown in Fig. 4B. Furthermore, the UV-Vis titration data of **1** with Cd^{2+} (Fig. 4C) was subjected to SPECFIT analysis[10] (Fig. S-17, ESI†), the result of which validates the 1 : 4 binding ratio and gives a binding constant of $\log\beta = 1.10 \pm 0.06$ M^{-4}.

In conclusion, we have found that incorporation of the "click"-generated triazole linker into the side chain of PPEs enables excellent fluorescence turn-on sensing function for Zn^{2+} and Cd^{2+} ions in THF, H$^+$ and Cd^{2+} ions in water. The remarkable sensitivity and selectivity displayed by sensors **PPE-1** and **PPE-4** bode well for a wide range of applicability; in particular, the water-soluble **PPE-4** is expected to be a useful sensor for Cd^{2+} ion detection in various applications.

This work was supported by NSERC, CFI, IRIF, and Memorial University of Newfoundland.

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