

Cyclodextrin-grafted poly(phenylene ethynylene) with chemically-responsive properties†

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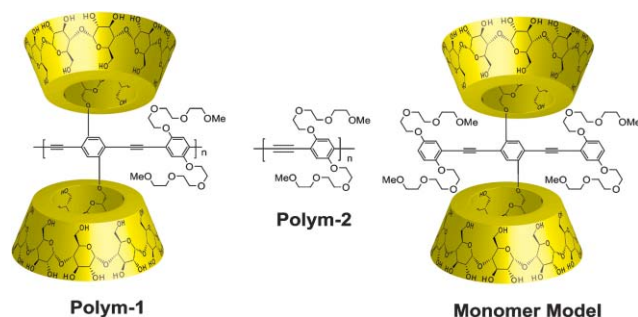
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Water-soluble poly(phenylene ethynylene) carrying β -cyclodextrin was prepared; the polymer exhibited a fluorescence color change or quenching, depending on the kind of guest.

Cyclodextrins (CDs) have received a great deal of interest because they selectively recognize guests such as aliphatic, aromatic and chiral compounds, and form complexes with these guests in aqueous solution.¹ Thus, CDs have been used for sensors, components of rotaxanes, polyrotaxanes and supramolecular polymers.²

π -Conjugated polymers are attracting significant interest because they are used in electrical conductivity, electroluminescence, light-emitting diodes and chemosensors.³ Among them, one of the current interests in the field of conjugated polymers focuses on the tuning of their optical and electrical properties by stimuli such as oxidation–reduction, pH and metal cations.⁴

Herein, we describe a water-soluble chemically-responsive fluorescent polymer employing CD; fluorescence color changes and quenching of the conjugated polymer are induced by host–guest complex formation in aqueous solution. We designed and synthesized β -CD modified poly(phenylene ethynylene) (**Polym-1**) via the Sonogashira coupling reaction (Scheme 1). As a reference for **Polym-1**, poly(phenylene ethynylene) without β -CD moieties (**Polym-2**) and a **Monomer Model** of **Polym-1** were also prepared (see ESI for experimental details†). **Polym-1** consists of a CD



Scheme 1 Chemical structure of **Polym-1**, **Polym-2** and the **Monomer Model**.

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† Electronic supplementary information (ESI) available: Experimental section, optical properties of polymers, concentration dependence of the fluorescence of **Polym-1** in aqueous solution, ¹H NMR spectra of **Polym-1** in D₂O and DMSO-*d*₆, molecular model of **Polym-1**, ¹H NMR spectra of **Polym-1** with AdCA and changes in fluorescence of **Monomer Model** upon addition of viologen derivatives. See DOI: 10.1039/b605804c

dimer unit; **Polym-1** is taken as a polymer of CD dimer, poly(CD dimer). To the best of our knowledge, the polymerization of CD dimer has not been reported. **Polym-1** is structurally interesting as each poly(phenylene ethynylene) is flanked by two CD groups. **Polym-1** is soluble in water, while **Polym-2** is insoluble in water. This is because the bulky hydrophilic CD groups of **Polym-1** increase its solubility.

Fig. 1(a) shows the absorption spectra of **Polym-1**, **Polym-2** and the **Monomer Model** in DMF; that of **Polym-1** being in aqueous solution. The absorption maximum of **Polym-1** in DMF was observed at 443 nm, while the spectrum of the **Monomer Model** exhibited peaks around 360 nm, indicating the expansion of π -conjugation along the polymer backbone. The absorption of **Polym-2** in DMF was almost same as that of **Polym-1**. In H₂O, the UV-vis absorption band of **Polym-1** red-shifted by about 30 nm and broadened. This peak shift indicates an increase in the conjugation length in aqueous solution by intermolecular π -stacking between π -conjugated polymer backbones.

Additional information regarding the effect of solvents on **Polym-1** comes from the emission spectra (Fig. 1(b)). In DMF, **Polym-1** exhibited a strong fluorescence (quantum yield: $\Phi_f = 0.24$), with emission at 481 nm. On the other hand, the fluorescence intensity decreased and the fluorescence peak was red-shifted with a fluorescence maximum at 493 nm ($\Phi_f = 0.07$) in H₂O, indicating the intermolecular π -stacking of polymer backbones in aqueous solution. By diluting a **Polym-1** aqueous solution, the fluorescence at 493 nm from aggregates decreased while fluorescence at 450 nm, derived from completely soluble **Polym-1**, appeared at the same time (ESI†). **Polym-1** is not completely soluble in its monomeric form but forms partially quenched aggregates in water. ¹H NMR studies in solution reveal further evidence of the intermolecular

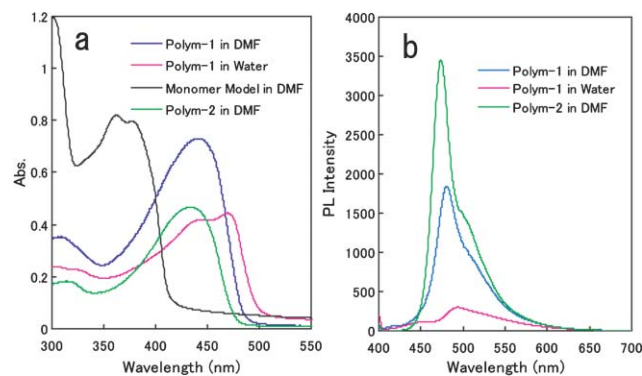


Fig. 1 (a) UV-vis and (b) emission spectra (excited at 400 nm) of **Polym-1**, **Polym-2** and **Monomer Model** (0.020 mM) in DMF and aqueous solutions.

π -stacking in aqueous solution (ESI†). The aromatic polymer backbone of **Polym-1** was observed in DMSO- d_6 but was not found in D $_2$ O, indicating the low rotational freedom of the aromatic polymer backbone segment in aqueous solution compared to in DMSO- d_6 . From molecular modelling studies of **Polym-1**, π - π stacking of the benzene part-modified β -CD was difficult due to steric hindrance by the β -CD moieties. On the other hand, the space around benzene group-modified triethylene oxide moieties was enough to form π - π stacking (see ESI on molecular modelling†).

Changes to optical properties by adding guest compounds to aqueous **Polym-1** solutions were investigated. With aliphatic 1-adamantanecarboxylic acid (**AdCA**) as a guest compound, the UV-vis absorption peak at 470 nm, derived from the stacking of π -conjugated polymer backbones, largely decreased and completely disappeared at 0.20 mM of **AdCA** (Fig. 2(a)). The emission with the peak at 490 nm, resulting from the intermolecular π -stacking between polymer chains, also decreased and a new emission peak around 460 nm appeared with increasing **AdCA** concentration (Fig. 2(b)). The emission color changed from light green ($\Phi_{fl} = 0.07$) to deep blue ($\Phi_{fl} = 0.11$) by addition of **AdCA** (Scheme 2, path (i)). In contrast, little change in UV-vis and emission spectra were found in the **Monomer Model** with **AdCA** (Fig. 2(c) and 2(d)). These observations indicate dissociation of the intermolecular π -stacking of polymer backbones by complexation of **AdCA** to the β -CD moieties of **Polym-1**.⁵ Repulsive forces between the complexed anions might prevent polymer chains from aggregating. The pH of the solution was neutral in the experiment, thus the proton of the carboxylic acid of **AdCA** should be

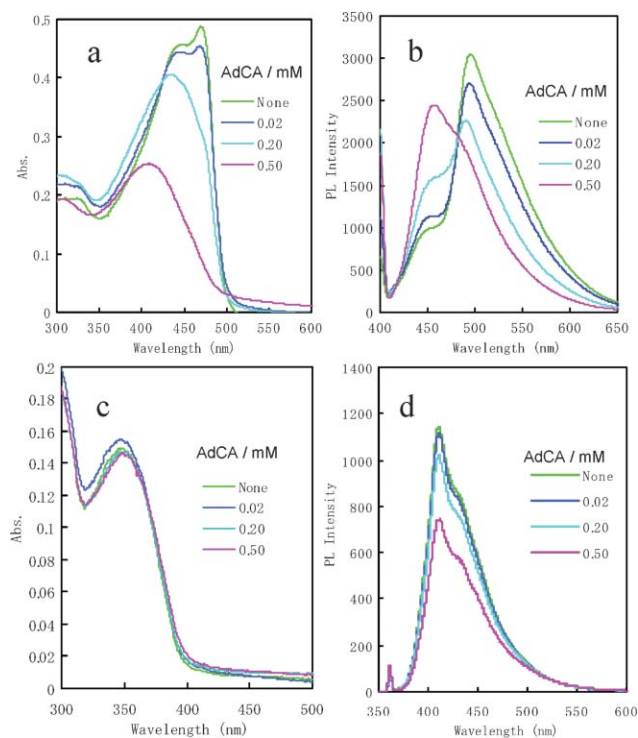
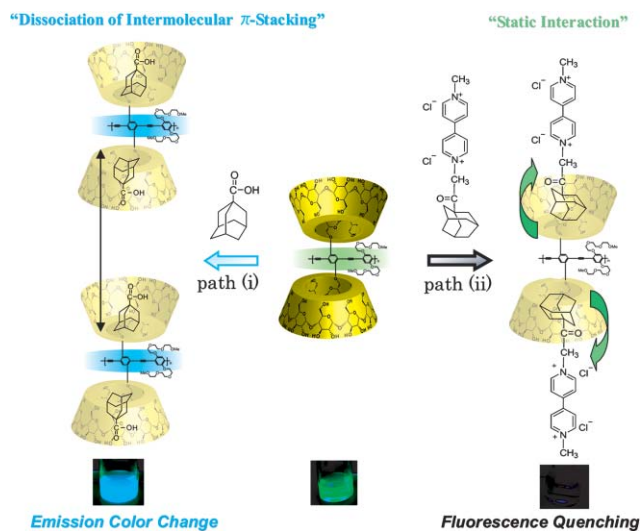


Fig. 2 (a) UV-vis and (b) emission spectral changes (excited at 400 nm) of aqueous **Polym-1** solutions (0.020 mM) by adding **AdCA**. (c) UV-vis and (d) emission spectral changes (excited at 360 nm) of aqueous **Monomer Model** solutions (0.020 mM) by adding **AdCA**.



Scheme 2 Changes in fluorescence induced by host-guest complexes.

dissociated. It is generally well known that carboxylic acid groups become carboxylate anions around pH 4–5.⁶

Fig. 3 shows the changes in fluorescence induced by adding viologen derivatives. It has been demonstrated that the fluorescence of poly(phenylene ethynylene)s is quenched by electron-accepting viologen groups.⁷ By adding an adamantane-modified viologen group (**AdBpyMe**), large scale fluorescence quenching was observed (Scheme 2, path (ii)). On the other hand, by using *N,N'*-dimethyl-4,4'-bipyridinium (**MeBpyMe**), low fluorescence quenching occurred because the cationic viologen group barely formed a host-guest complex with CD.⁸ These data indicate that the fluorescence quenching by adding **AdBpyMe** is due to inclusion complex formation between the adamantane moiety of **AdBpyMe** and the β -CD of **Polym-1**. Holding viologen groups on the side chain of **Polym-1** via host-guest formation results in efficient electron transfer from the poly(phenylene ethynylene) backbone to the viologen moiety of **AdBpyMe**. By using the **Monomer Model** instead of **Polym-1**, weak fluorescence quenching was observed upon addition of **AdBpyMe** (ESI†). These data indicate that the fluorescence quenching of **Polym-1** with **AdBpyMe** is amplified compared to that of the **Monomer Model**. Upon addition of an adamantane-bearing pyridinium moiety (**AdPy**) instead of

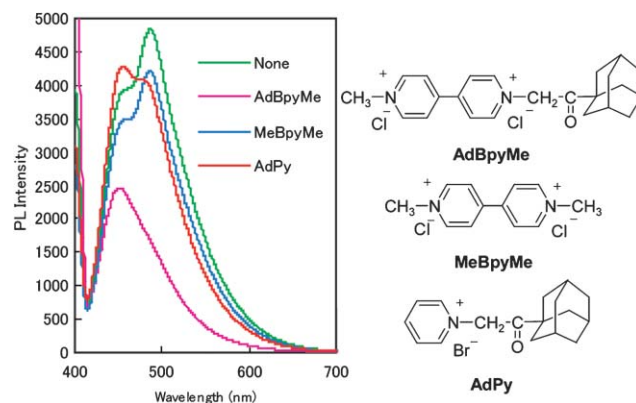


Fig. 3 Emission spectral changes (excited at 400 nm) of aqueous **Polym-1** solutions (0.020 mM) by adding viologen derivatives (0.20 mM).

AdBpyMe, the fluorescence quenching was not observed because the pyridinium group did not act as an electron-acceptor from poly(phenylene ethynylene)s.

In conclusion, the fluorescence of **Polym-1** was changed by the addition of guest compounds; the fluorescence color change and quenching of **Polym-1** occurred in aliphatic and acceptor guests, respectively (Scheme 2). The chemically-responsive fluorescence color change and quenching system in aqueous solution are interesting and little known. As the fluorescence changes take place in aqueous solution and the conjugated polymer backbone of **Polym-1** is surrounded by biocompatible CD moieties, there is promise that they will see application in molecular sensing drug-delivery systems (DDS).

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