Novel Reversible Chemosensory Material Based on Conjugated Side-Chain Polymer Containing Fluorescent Pyridyl Receptor Pendants

Hsuan-Chih Chu,[†] Yu-Hsien Lee,[‡] Shou-Jen Hsu,[†] Po-Jen Yang,[†] Atsushi Yabushita,[‡] and Hong-Cheu Lin*,[†]

[†]Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan
[‡]Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan

Ⓢ *Supporting Information*

ABSTRACT: A novel light-emitting monomer **M1** and its side-chain polymer **P1** containing three conjugated aromatic pendants, including one pyridyl terminus, were successfully synthesized via Wittig and Pd-catalyzed Heck coupling reactions. The fluorescence of polymer **P1** was efficiently quenched upon addition of different metal ions due to the facile energy transfers from the pendent groups of polymer **P1** to specific metal ions. Among these metal ions, **P1** exhibited extraordinary sensory selectivities for Ni^{2+} and Cu^{2+} ions over the other metal ions due to the stronger binding capabilities of Ni^{2+} and Cu^{2+} ions with polymer **P1**. From the time-resolved fluorescence (TRF) signals in photoluminescence spectra, the emergences of τ_1 decay components in polymer complexes (**P1**+Ni^{2+}) and (**P1**+Cu^{2+}) clearly indicated that their TRF traces consisted of two contributions, one from the complexes (τ_1) and the other from free polymer **P1** (τ_2). Upon addition of Ni^{2+} and Cu^{2+} ions, polymer **P1** showed faster decay time constants (τ_1) of metal ion quenching on TRF signals (i.e., better quenching efficiencies on photoluminescence) than its monomer **M1**. Furthermore, the on–off–on fluorescent switching behavior by adding a tridentate ligand 1,1,4,7,7-pentamethyl-diethylenetriamine (**PMDTA**) to the polymer complex (**P1**+Cu^{2+}) for several successive cycles demonstrated a superior reusable chemosensor of **P1** for further applications.
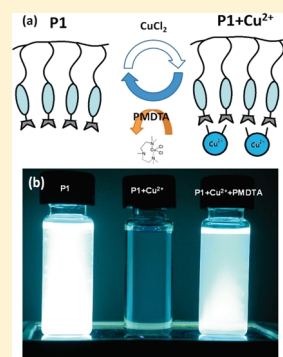
■ INTRODUCTION

Chemosensors by fluorescence detections have been studied widely and progressively in recent years owing to various applications in sensor technologies, such as pH values, metal ions, and biological species.[1−8] Specifically, conjugated polymer-based chemosensors have also attracted considerable attention because they offer observable fluorescence responses by the coupling interactions of their receptors with detecting analysts.[9−11] The multireceptor systems in polymers with collective interactions produce stronger responses than the respective monoreceptor systems in small molecules with single interactions. The anion and cation recognitions by chemosensors can be proceeded easily due to the sensitive and selective signal changes of colorimetry or fluorescence.[12−19] Lately, many fluorescent chemosensors (including small organic molecules and conjugated polymers) for metal ions were reported to have selective detections and also have been used in biological applications.[20−23] With regard to fluorescent chemosensors for copper ions (Cu^{2+}), several quenching effects of fluorescence intensities were evidently observed in the pyridyl chromophores to be binded with metal ions.[24−28] It is well understood that heavy metal ions tend to quench the luminescence of chromophores through electron and/or energy transfer processes, where the quenching behavior depends on the chelating capabilities of pyridyl ligands with metal ions to form complexes.[29−32] Generally, conjugated polymer-based chemosensors[28,33,34] with bipyridyl, terpyridyl, and

picolyl functional groups should contain plenty of receptors (due to polymeric structures) to trap the metal ions, and the pyridyl receptors linked properly with amide groups in suitable positions play an important role for the complexation of Cu^{2+} ions in a three-dimensional way.[18] In contrast to the single receptors of the monomers, the multireceptors of the corresponding conjugated polymers might be self-assembled to incorporate a large number of receptor units, which induce the transfer of excitation energy along the whole polymer backbones to the chromophore receptors and result in the amplification of fluorescent signals.[35] Moreover, the receptor structures of these conjugated molecules for chemosensors could also supply ligands to chelate the metal ions efficiently.[18,36] In the development of reversible fluorescent chemosensors, the sensor materials could not only provide the recognition species for sensing metal ions, but also possibly offer the on–off–on fluorescent switching for reuseable information processing.[37] To our knowledge, the on–off–on chemosensing responses of Cu^{2+} ions based on a conjugated side-chain polymer (**P1**) bearing pendent pyridyl termini are first developed in this study, where the reversible emissions of the quenched sensor polymer complexes with Cu^{2+} ions could be recovered several times by rechelating Cu^{2+} ions with the consecutive addition of

Scheme 1. Schematic Representation of Monomer M1 and Polymer P1 Bearing Pyridyl Termini as Metal Ion Receptors
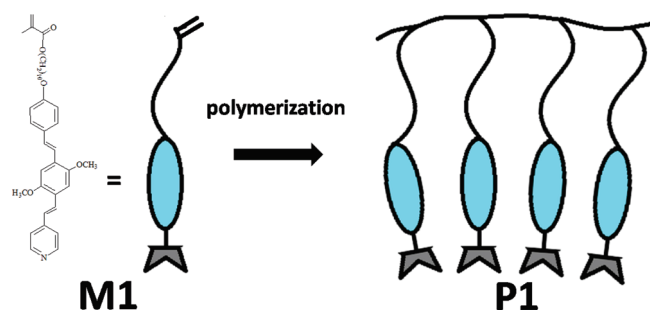
the tridentate ligand 1,1,4,7,7-pentamethyldiethylenetriamine (**PMDTA**).

Herein, we design and synthesize a conjugated monomer and its homopolymer with pyridyl pendants as receptors for the chemosensor applications of detecting analysts. The formation of a complex through a pyridyl-*N*-metal coordination and the detection of the corresponding fluorescent properties provided us with a model of both monomer and its conjugated side-chain polymer to recognize metal ions in this study. On the basis of the fluorescence responses, the conjugated polymer demonstrated a more effective chemosensor capability to distinguish the presence of Cu^{2+} ions selectively and reversibly compared with its single pyridyl-functionalized monomer. As shown in Scheme 1, monomer **M1** containing three conjugated aromatic rings, including one pyridyl terminus and two lateral methoxyl groups (on the middle ring), was successfully synthesized via Wittig and Pd-catalyzed Heck coupling reactions, and then **M1** was polymerized to yield conjugated polymer **P1** by free radical polymerization.[38]

EXPERIMENTAL SECTION

Materials. Chemicals and solvents were reagent grade and purchased from Aldrich, ACROS, TCI, and Lancaster Chemical Co. Tetrahydrofuran (THF) and triethylamine (Et_3N) were distilled to keep anhydrous before use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. The other chemicals were used without further purification.

Synthesis of Monomer M1 (2-Methyl-acrylic Acid 10-(4-{2-[2,5-Dimethoxy-4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenoxy)-decyl ester). The detailed synthetic procedures of the receptor monomer (**M1**) are described in the Supporting Information (ESI†). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.56 (d, J = 6.0 Hz, 2H), 7.68 (d, J = 16.2 Hz, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 6.0 Hz, 2H), 7.34 (d, J = 16.5 Hz, 1H), 7.13 (s, 1H), 7.12 (s, 1H), 7.09 (d, J = 16.5 Hz, 1H), 7.02 (d, J = 16.5 Hz, 1H), 6.89 (d, J = 8.7 Hz, 2H), 6.09 (s, 1H), 5.54 (s, 1H), 4.14 (t, J = 6.6 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 1.94 (s, 3H), 1.84–1.74 (m, 2H), 1.72–1.63 (m, 2H), 1.46–1.25 (m, 12H). HRMS (EI): calcd for $C_{37}H_{45}NO_5$, 583.32977; found 583.3297. Anal. Calcd for $C_{37}H_{43}NO_5$: C, 76.13; H, 7.77; N, 2.40. Found: C, 76.02; H, 7.77; N, 2.54.

Measurements and Characterization. ^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. High-resolution electron impact mass data were obtained on a Finnigan-MAT-95XL. Gel permeation chromatography (GPC) analysis was equipped with a Waters HPLC pump 510 connected to a Waters 410 differential refractmeter and three Ultrastyragel columns using polystyrene as a standard and THF as an eluant. UV–vis absorption spectra were recorded on a HP G1103A spectrophotometer, and photoluminescence (PL) spectra were obtained on a Hitachi F-4500 spectrophotometer in dilute THF solutions (10^{-6} M). Time-resolved photoluminescence (TRPL) spectra were measured using a home-built single photon counting system. Excitation was performed using a 375 nm diode laser (Picoquant PDL-200, 50 ps fwhm, 2 MHz). The signals collected at the excitonic emissions of solutions (λ = 480 nm) were connected to a time-correlated single photon counting card (TCSPC, Picoquant Timeharp 200). The emission decay data were analyzed with the biexponential kinetics in which two decay components were derived. The lifetime values (τ_1 and τ_2) and pre-exponential factors (A_1 and A_2) were determined and summarized.

Synthesis of Polymer P1. The polymerization was carried out by a free radical polymerization described as follows: In a Schlenk tube, 1.0 g (1.7 mmol) monomer **M1** was dissolved in dried THF (7.5 mL), and AIBN (2 mol % of total monomer concentration) was added as an initiator. The acquired solution was degassed by three freeze–pump–thaw cycles, and then the Schlenk tube was sealed off. The reaction mixture was stirred and heated at 60 °C for 24 h. After polymerization, the polymer was precipitated with diethyl ether. The precipitated polymer was collected, washed with diethyl ether, and dried under vacuum. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.44 (br, 2H), 7.53–6.77 (m, 12H), 3.80 (br, 10H), 1.66–1.24 (br, 21H).

Metal Ion Titration. Metal ion titration experiments were started with 150 mL of polymer **P1** in THF solutions with a known concentration (5.0×10^{-6} M). Solutions of metal salts (chlorate salts 1×10^{-3} M in THF containing 3% H_2O) were used for the titration. The fluorescence titration data were taken 7 min prior to measuring fluorescence spectra, which allowed for the complete formation of the complexes between the ions and the polymer.

RESULTS AND DISCUSSION

Syntheses and Characterization of Monomer (M1) and Polymer (P1). The synthetic routes of monomer **M1** were followed by several reactions as outlined in Scheme 2. The key steps to form three-conjugated rings of the receptor emitter monomer **M1** were designed on the basis of Wittig and Pd-catalyzed Heck coupling reactions. Compound **1** was protected at one hydroxyl group of terminus decyloxy chain with *tert*-butyldimethylsilyl chloride (TBDMSCl) to give compound **2**. The aldehyde group of compound **2** was further converted to a derivative vinyl group of compound **3** by Wittig reaction under the methyl triphenylphosphonium bromide treatment. Compound **4** was obtained by a six-step synthetic path from 2,5-dimethoxybenzaldehyde according to our previous report.[38b] Compound **5** was prepared by means of Pd-catalyzed Heck coupling reaction between compounds **3** and **4** with $Pd(OAc)_2$ as a catalyst in the presence of $P(o$-tolyl$)_3$ in Et_3N/THF (1/1, v/v), which was then deprotected with tetra-*n*-butylammonium fluoride (TBAF) in THF to acquire compound **6**. Finally, monomer **M1** (**7**) was obtained by transesterification reaction between compound **6** and an excess amount (2.5 equiv) of vinyl methacrylate in the presence of a higher concentration of

**Scheme 2. Synthetic Procedures of Monomer M1 and Polymer P1**
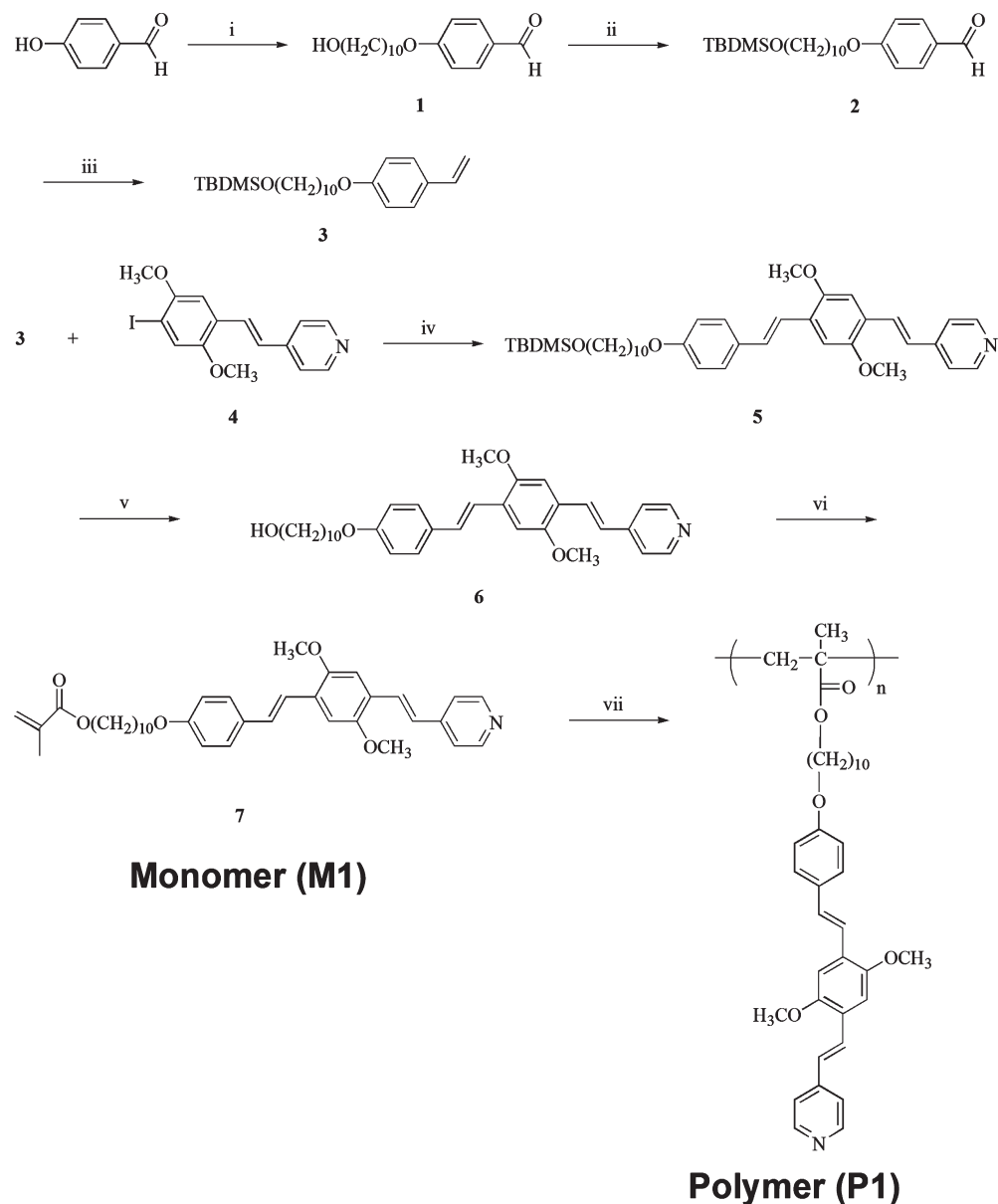
Reagents and reaction conditions: (i) 10-bromodecanol, K_2CO_3, KI, butan-2-one, reflux, 48 h; (ii) TBDMSCl, CH_2Cl_2, room temperature, 10 h; (iii) methyltriphenylphosphonium bromide, t-BuOK, THF, room temperature, 4 h; (iv) Pd(OAc)$_2$, P(o-tolyl)$_3$, Et$_3$N/THF (1/1, v/v), 100 °C, 12 h; (v) TBAF, THF, 40 °C, overnight; (vi) vinyl methacrylate, 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane, 2,6-ditert-butyl-4-methylphenol, THF, 50 °C, 48 h; (vii) AIBN, THF, 60 °C, 24 h.

1,3-dichloro-1,1,3,3-tetrabutyldistannoxane as a catalyst and 2,6-ditert-butyl-4-methylphenol as an inhibitor in THF. The final chemical structure of monomer **M1** was confirmed by ^{1}H NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis.

The homopolymerization of monomer **M1** was performed by a conventional approach of free radical polymerization in THF at 60 °C with AIBN as an initiator. Polymer **P1** was obtained as an orange-yellow solid after purification (with a yield of 65%) and can be readily soluble in organic solvents, such as THF, dimethyl sulfoxide (DMSO), and N,N-dimethylformamide (DMF). A number-average molecular weight (M_n) of 11200 g/mol in **P1** was determined by GPC using THF eluent with a calibration

curve of polystyrene standards, and a corresponding degree of polymerization ca. 19 with a polydispersity index (PDI) of 1.7 was obtained.

In order to verify the chemical structure of polymer **P1**, the ^{1}H NMR spectroscopy of **P1** (in d-THF) was compared with that of its monomer **M1** (in CDCl$_3$). The coupling constant of the vinyl protons in monomer **M1** was in the range of 16.2−16.5 Hz, which was consistent with the expected value for an all-$trans$ configuration. The chemical shifts of polymer **P1** were characterized as the same positions as those of monomer **M1**, except for the broadening of some characteristic peaks and the disappearance of the vinyl (methacrylate) groups at peaks ca. 5.4−6.1 ppm, indicating that the monomers were completely reacted after homopolymerization.
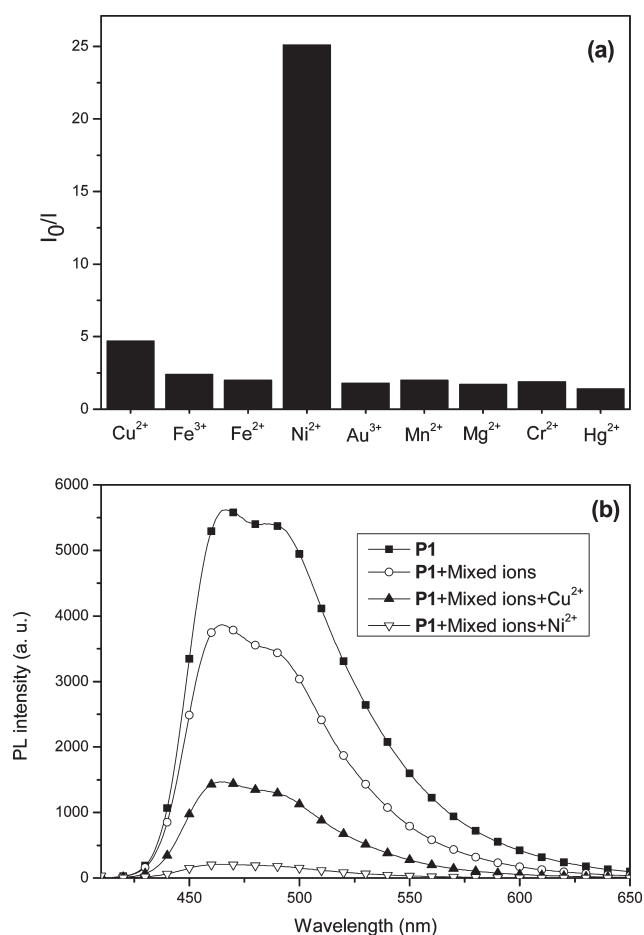
Figure 1. (a) PL quenching profiles of **P1** solutions (5.0×10^{-6} M in THF) by various metal ions (Cu^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Au^{3+}, Mn^{2+}, Mg^{2+}, Cr^{2+}, and Hg^{2+}). (b) Fluorescence quenching response of **P1** solutions (5×10^{-6} M in THF) by Ni^{2+} (1.1×10^{-6} M) and Cu^{2+} (2.5×10^{-6} M) mixed with the other combined metal ions (2.8×10^{-6} M for each metal ion: Fe^{3+}, Fe^{2+}, Au^{3+}, Mn^{2+}, Mg^{2+}, Cr^{2+}, and Hg^{2+}), where the excitation wavelength was 400 nm.

PL Titration Spectra of Metal Ions. In order to verify the selectivity of the synthesized chemosensors, including monomer **M1** and polymer **P1**, a variety of metal ions (Cu^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Au^{3+}, Mn^{2+}, Mg^{2+}, Cr^{2+}, and Hg^{2+}) were tested. As shown in Figure 1a, the relative fluorescence intensities (I_0/I) of the conjugated polymer **P1** were detected before and after complexation with different metal ions. With respect to the other metal ions, only Cu^{2+} and Ni^{2+} ions could quench the fluorescence of **P1** more effectively even at very low concentrations. The influences of the other metal ions on the sensing capabilities of Ni^{2+} and Cu^{2+} ions were also evaluated. Due to the poor coordination abilities of the pyridyl receptor with these metal ions other than Ni^{2+} and Cu^{2+}, a partial quenching phenomenon of **P1** was observed by mixing with the other combined metal ions (2.8×10^{-6} M for each metal ion: Fe^{3+}, Fe^{2+}, Au^{3+}, Mn^{2+}, Mg^{2+}, Cr^{2+}, and Hg^{2+}) in Figure 1b. Moreover, the fluorescence of **P1** could be further quenched sufficiently by adding Ni^{2+} (1.1×10^{-6} M) and Cu^{2+} (2.5×10^{-6} M) metal ions, respectively. Therefore, **P1** could act as an efficient chemosensor for the detection of Ni^{2+} and Cu^{2+} ions without disturbance from the other combined metal ions. Compared with the relative changes of fluorescence intensities at a low concentration of 2.5×10^{-6} M in Figure 2a,
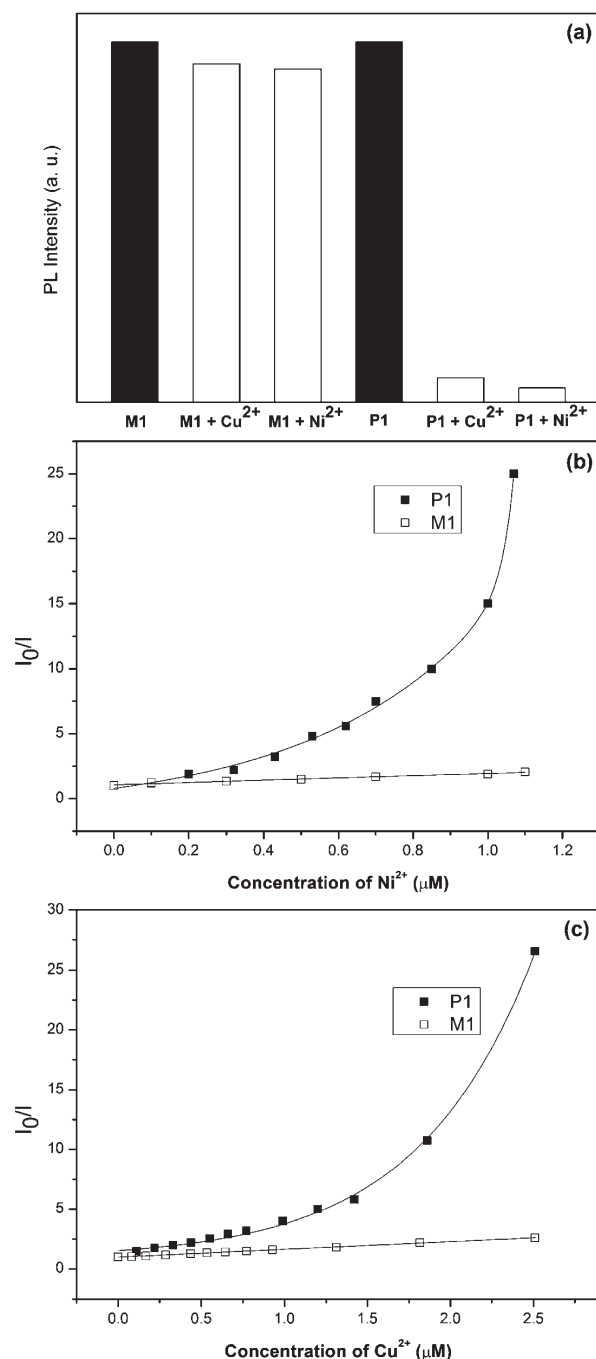
Figure 2. (a) Relative PL spectra of monomer (**M1**) and polymer (**P1**) upon addition of $NiCl_2$ and $CuCl_2$ in THF solutions (2.5×10^{-6} M) with an excitation at 400 nm. (b) Stern−Volmer plots of **M1** and **P1** in the presence of different fluorescence responses upon increasing Ni^{2+} concentrations. (c) Stern−Volmer plots of **M1** and **P1** in the presence of different fluorescence responses upon increasing Cu^{2+} concentrations.

the quenching effects of monomer **M1** by metal ions could not be comparable with those of polymer **P1** by Cu^{2+} and Ni^{2+} ions, respectively. These phenomena demonstrated that **P1** displayed the best quenching selectivity for Ni^{2+} ion and next for Cu^{2+} ion. As shown in Table 1, the PL-quenching efficiencies can be calculated from the static Stern−Volmer quenching constants (K_{sv}) through monitoring the corresponding decreases of PL intensities by increasing the metal ion concentrations in the

8848

dx.doi.org/10.1021/jp201586c |*J. Phys. Chem. B* 2011, 115, 8845–8852

Table 1. Stern−Volmer Quenching Constants (K_{SV}) of P1 for Different Metal Ions

metal ion	$K_{SV}{}^{a}$ (M^{-1})
Cu^{2+}	2.82×10^6
Fe^{3+}	1.27×10^6
Fe^{2+}	9.23×10^5
Ni^{2+}	5.65×10^6
Au^{3+}	7.51×10^5
Mn^{2+}	8.74×10^5
Mg^{2+}	6.63×10^5
Cr^{2+}	8.05×10^5
Hg^{2+}	3.18×10^5

^{a} The PL-quenching efficiency can be evaluated by the static Stern−Volmer equation: $I_0/I = 1 + K_{SV} [Q]$ where I_0 is the PL intensity in the absence of the quencher, I is the PL intensity in the presence of the quencher, K_{SV} is the Stern−Volmer quenching constant, and $[Q]$ is the quencher concentration.

linear region of Figure 2b,c. The K_{sv} value of Ni^{2+} ion ($5.65 \times 10^6\,M^{-1}$) is 2 times higher than that of Cu^{2+} ion ($2.82 \times 10^6\,M^{-1}$), which indicates that Ni^{2+} and Cu^{2+} ions have much stronger coordination bindings to **P1** than the other metal ions.

Comparing the PL-quenching sensitivities of polymer **P1** and its monomer **M1**, their quenching characteristics toward Ni^{2+} and Cu^{2+} ions could be distinguished, because the metal ion-coordinating capabilities of pyridyl termini as receptors in the monomer and polymer led to different coordination strengths. Upon addition of Ni^{2+} and Cu^{2+} ions (with the same concentrations of $1.1 \times 10^{-6}\,M$ for Ni^{2+} and $2.5 \times 10^{-6}\,M$ for Cu^{2+} to **P1** and **M1**, respectively) in Figure 2a, a relatively weaker and incomplete PL-quenching feature of monomer **M1** was observed in contrast to that of polymer **P1**. As quenched by Ni^{2+} ions to the highest extent in Figure 2b, about a 6-fold enhanced static Stern−Volmer constant ($K_{SV} = 5.65 \times 10^6\,M^{-1}$) of polymer **P1** was observed relative to that ($K_{SV} = 8.57 \times 10^5\,M^{-1}$) of its monomer **M1**. Figure 2c demonstrated similar results as quenched by Cu^{2+} ions, where polymer **P1** also exhibited a much larger quenching efficiency ($K_{SV} = 2.89 \times 10^6\,M^{-1}$) than monomer **M1** ($K_{SV} = 4.77 \times 10^5\,M^{-1}$). Due to both larger quenching efficiencies of **P1** by Ni^{2+} and Cu^{2+} ions (in comparison with **M1**), it is clearly evident that the pyridyl groups of **P1** could be complexed with Ni^{2+} and Cu^{2+} ions more easily than those of **M1**. In general, the side-chain polymer system possessing higher quenching constants than the monomer was believed to be caused by the synergistic summation for all pendant receptor units in the conjugated side-chains of polymer **P1**. While the discrete receptors of monomers (**M1**) were associated with the upcoming metal ions individually, the PL emissions of monomers with separated pyridyl groups were partially quenched. Therefore, this highly sensitive conjugated polymer exhibited more apparent sensory signal responses over its monomer.

TRPL Spectra. Previous research reported that heavy metal ions tend to quench the luminescence of conjugated receptors, including polymers and monomers by electron-transfer and energy-transfer processes.[38−40] The time-resolved fluorescence (TRF) signals of **M1** and its complexes (**M1**+Cu^{2+} and **M1**+Ni^{2+}) probed at 480 nm with an excitation at 375 nm are shown in Figure 3a. The result revealed that ligation of monomers with metal ions ($2.5 \times 10^{-6}\,M$) did not quench PL of **M1** efficiently. TRF traces of **P1** in the absence/presence of metal ions are
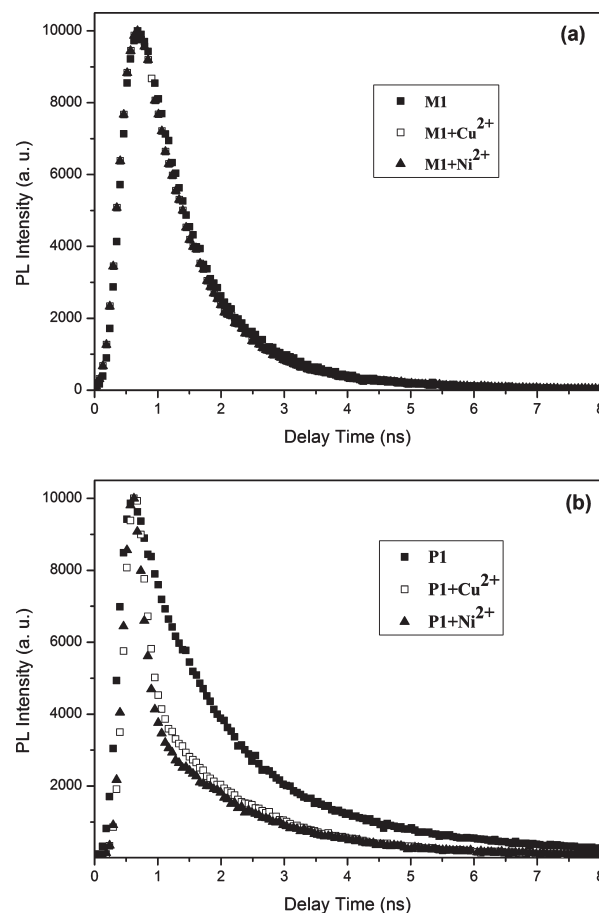

Figure 3. (a) TRF of **M1** (solid squares), **M1**+Cu^{2+} (open squares) and **M1**+Ni^{2+} (solid triangles); (b) TRF of **P1** in the absence (solid squares) and in the presence of Cu^{2+} (open squares) and Ni^{2+} (solid triangles) ions. The concentrations of **M1** and **P1** were $5 \times 10^{-6}\,M$ dissolved in THF solutions containing different metal ions ($2.5 \times 10^{-6}\,M$).

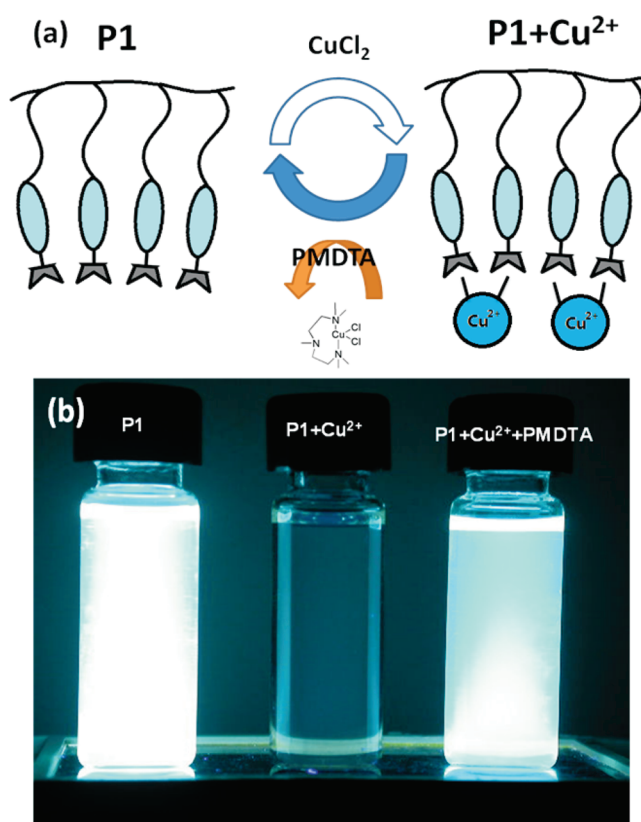**Table 2. Fluorescence Decay Time Constants of P1 and M1 in the Presence of Cu^{2+} and Ni^{2+} Ions**

	A_1	τ_1 (ns)	A_2	τ_2 (ns)
P1			100%	1.375
P1+Cu^{2+}	72.2%	0.197	27.8%	1.616
P1+Ni^{2+}	78.8%	0.131	21.2%	1.578
M1			100%	1.644
M1+Cu^{2+}			100%	1.468
M1+Ni^{2+}			100%	1.496

plotted in Figure 3b, illustrating that Cu^{2+} and Ni^{2+} ions could affect the fluorescence lifetime values of **P1**. Their fluorescence lifetimes obtained by deconvolution of instrumental response function[42] and exponential fittings are summarized in Table 2. In the absence of Cu^{2+} and Ni^{2+} ions, single exponential fitting estimated the fluorescence lifetime of **P1** as 1.375 ns, which corresponded to the lifetime of the S1 state. Adding metal ions to the solutions, an ultrafast decay time constant (τ_1) appeared in the results of biexponential decay fittings. The ratio of the faster decay component increased up to 72.2% with Cu^{2+} ions and to 78.8% with Ni^{2+} ions, which reflected different interactions between **P1** and various metal ions. More importantly, the longer decay
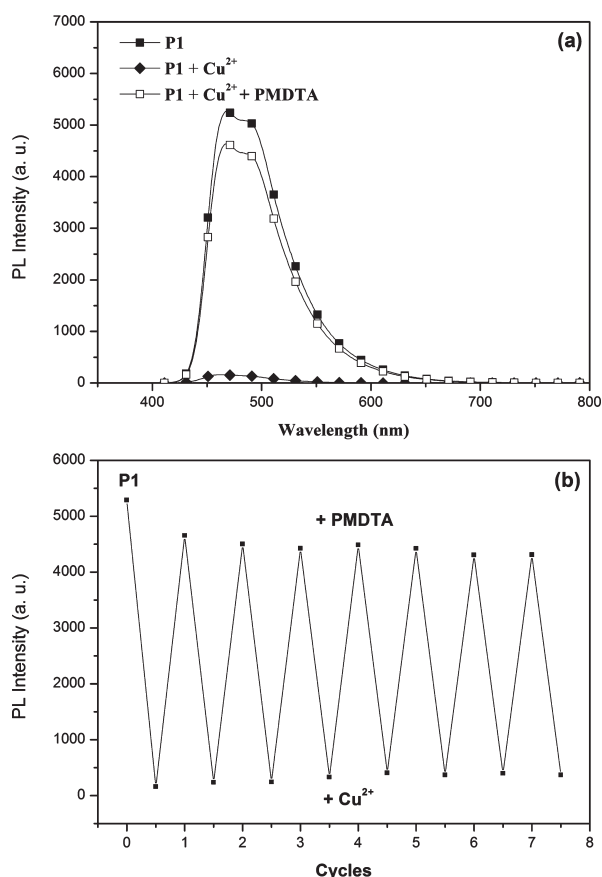
Figure 4. (a) PL spectra of polymer **P1** $(5 \times 10^{-6} \text{ M})$ in THF solutions before and after the addition of Cu^{2+}, and recovered upon the addition of **PMDTA** $(2.5 \times 10^{-6} \text{ M})$. Excitation wavelength was at 400 nm. (b) The switches of on−off−on fluorescent spectra for seven successive cycles.

Figure 5. (a) The reversible conversion cycle of **P1** $(5 \times 10^{-6} \text{ M})$ in the presence of Cu^{2+} ions $(2.5 \times 10^{-6} \text{ M})$ and **PMDTA** $(2.5 \times 10^{-6} \text{ M})$; (b) Photographs of initial PL emission for **P1**, quenched PL emission for polymer complex (**P1**+Cu^{2+}), and PL re-emission for polymer complex (**P1**+Cu^{2+}) upon adding **PMDTA** (i.e., for **P1**+Cu^{2+}+**PMDTA**).

time constant (τ_2) of **P1** continued to exist (27.8% and 21.2% for Cu^{2+} and Ni^{2+} ions, respectively) even if metal ions were added to the solutions. The emergence of the τ_1 decay component in **P1**+Cu^{2+} and **P1**+Ni^{2+} clearly indicated that their TRF traces consisted of two contributions: one from free **P1** (τ_2) and another from its complex (τ_1). The quenches of TRF signals upon addition of metal ions implied that the metal ions formed a charge-transfer emitting state with **P1**. In the absence of Cu^{2+} and Ni^{2+} ions for monomer **M1**, single exponential fitting estimated the fluorescence lifetime of **M1**. From Table 2, Cu^{2+} and Ni^{2+} ions could not affect the fluorescence delay time of **M1** sufficiently. The delay time of the original decay component could be approximately 100% upon adding metal ions.[41] Apparently, the interactions of **P1** with metal ions (Cu^{2+} and Ni^{2+} ions) created another fluorescence quenching pathways in which the photoexcited energy of the pyridyl receptors effectively transfer from the conjugated side chains to the metal ions (Ni^{2+} and Cu^{2+}). The observed fluorescence quenching phenomena of the ligands were thought to reflect the excitation energy transfer from the ligands to the metal d-orbital.[39,40] Comparing the fluorescence quenching efficiencies of the metal ions for **P1** and **M1**, the formation of a complex through a pyridyl-N-metal coordination and the detection of the corresponding fluorescent quenching behavior provided a tool for us to construct a model of both single molecule and conjugated side-chain polymer to recognize metal ions. By utilizing the collective characteristics

of the polymer configuration containing multiple pyridyl-receptors, one could achieve enhanced sensitivity of fluorescent polymer sensors relative to monomer sensors.

PL-Quenching Reversibility of P1 in the Application of On−Off−On Chemosensors for Cu²⁺ Ions. In order to use the chemosensor polymers reversibly, the reemissions of the quenched sensor polymers (complexed with metal ions) could be successively recovered by rechelating of the metal ions to another competing ligand with a stronger binding force. For instance, Cu^{2+} ions can interact with an amino tridentate ligand of **PMDTA**, which offers a chelating ring with a σ-donating character, to form copper(II) complexes.[43] Compared with **P1**, **PMDTA** has better binding capability with Cu^{2+}, so Cu^{2+} ions in the quenched complex (**P1**+Cu^{2+}) could be taken away by the tridentate ligand (**PMDTA**) easily and transformed into a more stable complex (**PMDTA**+Cu^{2+}). Therefore, by adding **PMDTA** into the previously quenched polymer complex (**P1**+Cu^{2+}) solution, a substituted complex (**PMDTA**+Cu^{2+}) were generated to release polymer **P1** with the reversible sensing capability (e.g., Cu^{2+} ions), which could be beneficial to be utilized for on−off-on chemosensors. To investigate this chemosensing reversibility, the fluorescence of **P1** in complex (**P1**+Cu^{2+}) could be recovered upon the addition of **PMDTA** in an equivalent molar concentration of Cu^{2+} ions. As shown in Figure 4a, the fluorescence of **P1** was quenched upon adding Cu^{2+}, but **P1** could recover 80% of its original PL intensity upon the addition of **PMDTA** to the quenched complex (**P1**+Cu^{2+}) solution. Obviously, the

8850

dx.doi.org/10.1021/jp201586c |*J. Phys. Chem. B* 2011, 115, 8845–8852
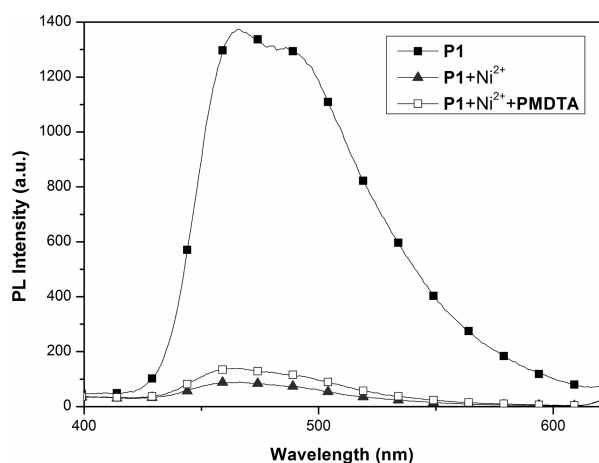
Figure 6. PL spectra of polymer **P1** (5×10^{-6} M) in THF solutions before and after the addition of Ni^{2+} (1.1×10^{-6} M), and barely recovered upon the addition of **PMDTA** (2.5×10^{-6} M), where the excitation wavelength was 400 nm.

fluorescence-recovered **P1** could be quenched again by further adding Cu^{2+} ions, and the fluorescence of **P1** might be restored over 95—100% steadily (or ~80% of the original PL intensity in **P1** first) upon repeatedly adding **PMDTA**.

As shown in Figure 4b, the **P1**-based chemosensor shows excellent stability with no observable decayed PL signals for seven successive cycles, which is important for the practical applications of chemosensors. A reversible chemosensing example of complex (**P1**+Cu^{2+}) is revealed in Figure 5a, which demonstrates an on—off-on fluorescent switching process upon adding **PMDTA** in Figure 5b. However, although a larger PL quenching effect of **P1** by Ni^{2+} ions was observed, the quenched fluorescence of complex (**P1**+Ni^{2+}) was only 10% recovered (relative to **P1**'s original PL intensity) upon the addition of the tridentate ligand **PMDTA** (Figure 6). Due to the stronger binding of **P1** with Ni^{2+} than **PMDTA**, Ni^{2+} ions in polymer complex (**P1**+Ni^{2+}) could not be rechelated back to **PMDTA**, so polymer **P1** could not be developed as reversible fluorescence sensors for Ni^{2+} ions. Owing to the stronger Ni^{2+} binding with **P1** than Cu^{2+} ions, the quenched PL emission in polymer complex (**P1**+Ni^{2+}) solution could not be turned on again after addition of **PMDTA**. Therefore, by sequentially adding **PMDTA** ligands, the reversible chemosensor applications of polymer **P1** are only pertinent to Cu^{2+} ions (rather than Ni^{2+} ions), because of the moderate binding force of **P1** with Cu^{2+} ions.

CONCLUSION

Chemosensory monomer **M1** and its conjugated side-chain polymer **P1** containing three conjugated aromatic pendants (including one pyridyl terminus) were successfully synthesized. The PL intensities of polymer **P1** were more efficiently quenched upon addition of Ni^{2+} and Cu^{2+} than the other metal ions due to the stronger binding capabilities of Ni^{2+} and Cu^{2+} ions with pyridyl receptors of **P1**. According to the TRF signals in PL spectra, the PL quenching efficiencies of side-chain polymer **P1** and monomer **M1** were compared by adding various metal ions to indicate that polymer **P1** had smaller lifetime τ_1 values and possessed better PL quenching efficiencies to recognize Ni^{2+} and Cu^{2+} metal ions. The on—off—on fluorescent switching behavior upon addition of **PMDTA** to polymer complex (**P1**+Cu^{2+})

demonstrated a superior reusability of the chemosensor polymer (**P1**). However, this chemosensory polymer (**P1**) for Cu^{2+} detection could not be utilized in aqueous solutions, in which the chemosensory polymer should be adjusted to become water-soluble by adding some hydrophilic moieties. Most importantly, the chemosensory selectivity and reversibility in the conjugated pyridyl side-chains of polymer **P1** may also be extended to other water-soluble polymers and could be potentially led to new sensor applications for novel biological systems.

ASSOCIATED CONTENT

S **Supporting Information.** Text giving experimental details and characterization of **M1** and PL emission response spectra of polymer P1 in THF solutions titrated with various metal ions. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Address: Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan (ROC). Tel: 8863-5712121 ext. 55305. Fax: 8863-5724727. E-mail: linhc@cc.nctu.edu.tw.

ACKNOWLEDGMENT

REFERENCES

(1) (a) Yang, H.; Liu, Z. Q.; Zhou, Z. G.; Shi, E. X.; Li, F. Y.; Du, Y. K.; Yi, T.; Huang, C. H. *Tetrahedron Lett.* **2006**, *47*, 2911–2914. (b) Zhou, G.; Cheng, Y.; Wang, L.; Jing, X.; Wang, F. *Macromolecules* **2005**, *38*, 2148–2153. (c) Zhang, Y.; Murphy, C. B.; Jones, W. E. *Macromolecules* **2001**, *35*, 630–636. (d) Bandyopadhyay, P.; Ghosh, A. K. *J. Phys. Chem. B* **2010**, *114*, 11462–11467. (e) Author, A.; Coauthor, B. *Chem.—Eur. J.* **2001**, *7*, 1–10. (f) Author, A.; Coauthor, B. *Angew. Chem.* **2006**, *118*, 1–5. (g) Lee, Y.; Liu, H.; Lee, J.; Kim, S.; Sessler, J.; Kim, Y.; Kim, J. *Chem.—Eur. J.* **2010**, *16*, 5895–5901.

(2) (a) Wen, Z. C.; Yang, R.; He, H.; Jiang, Y. B. *Chem. Commun.* **2006**, 106–108. (b) Sanchez, J. C.; Urbas, S. A.; Toal, S. J.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Macromolecules* **2008**, *41*, 1237–1245. (c) Fan, L. J.; Jones, W. E. *J. Phys. Chem. B* **2006**, *110*, 7777–7782.

(3) (a) Royzen, M.; Durandin, A.; Young, V. G.; Geacintov, N. E.; Canary, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 3854–3855. (b) Shiraishi, Y.; Kohno, Y.; Hirai, T. *J. Phys. Chem. B* **2005**, *109*, 19139–19147. (c) Liu, Y.; Zhang, S.; Miao, Q.; Zheng, L.; Zong, L.; Cheng, Y. *Macromolecules* **2007**, *40*, 4839–4847. (d) Mancin, F.; Rampazzo, E.; Tecilla, P.; Tonellato, U. *Chem.—Eur. J.* **2006**, *12*, 1844–1854.

(4) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419–4476.

(5) Manoj, P.; Min, C. K.; Aravindakumar, C. T.; Joo, T. *Chem. Phy.* **2008**, *352*, 333–338.

(6) (a) Lee, H. N.; Xu, Z.; Kim, S. K.; Swamy, K. M. K.; Kim, Y.; Kim, S. J.; Yoon *J. Am. Chem. Soc.* **2007**, *129*, 3828–3829. (b) Park, Y.; Apodaca, D. C.; Pullen, J.; Advincula, R. C. *J. Phys. Chem. B* **2010**, *114*, 13084–13094. (c) Liu, B.; Yu, W. L.; Pei, J.; Liu, S. Y.; Lai, Y. H.;

Huang, W. *Macromolecules* **2001**, *34*, 7932–7940. (d) Zahn, S.; Proni, G.; Spada, G.; Canary, J. *Chem.—Eur. J.* **2001**, *7*, 88–93.

(7) Kim, J. S.; Quang, D. T. *Chem. Rev.* **2007**, *107*, 3780–3799.

(8) Basabe-Desmonts, L.; Reinhoudt, D. N.; Crego-Calama, M. *Chem. Soc. Rev.* **2007**, *36*, 993–1017.

(9) Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W. E. *J. Phys. Chem. B* **2004**, *108*, 1537–1543.

(10) Guo, Z.; Zhu, W.; Xiong, Y.; Tian, H. *Macromolecules* **2009**, *42*, 1448–1453.

(11) Fan, L. J.; Jones, W. E. *J. Am. Chem. Soc.* **2006**, *128*, 6784–6785.

(12) Swamy, K. M. K.; Ko, S. K.; Kwon, S. K.; Lee, H. N.; Mao, C.; Kim, J. M.; Lee, K. H.; Kim, J.; Shin, I.; Yoon, J. *Chem. Commun.* **2008**, 5915–5917.

(13) Suresh, M.; Ghosh, A.; Das, A. *Chem. Commun.* **2008**, 3906–3908.

(14) Royzen, M.; Dai, Z.; Canary, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 1612–1613.

(15) Liu, T.; Hu, J.; Yin, J.; Zhang, Y.; Li, C.; Liu, S. *Chem. Mater.* **2009**, *21*, 3439–3446.

(16) Kim, H. N.; Lee, M. H.; Kim, H. J.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2008**, *37*, 1465–1472.

(17) Kaur, N.; Kumar, S. *Chem. Commun.* **2007**, 3069–3070.

(18) Jung, H. S.; Kwon, P. S.; Lee, J. W.; Kim, J. I.; Hong, C. S.; Kim, J. W.; Yan, S. H.; Lee, J. Y.; Lee, J. H.; Joo, T.; Kim, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 2008–2012.

(19) (a) Geng, J.; Kong, B. S.; Yang, S. B.; Youn, S. C.; Park, S.; Joo, T.; Jung, H. T. *Adv. Funct. Mater.* **2008**, *18*, 2659–2665. (b) Li, Z. a.; Lou, X.; Yu, H.; Li, Z.; Qin, J. *Macromolecules* **2008**, *41*, 7433–7439. (c) Chen, Y.; Li, F.; Bo, Z. *Macromolecules* **2010**, *43*, 1349–1355. (d) Amara, J. P.; Swager, T. M. *Macromolecules* **2005**, *38*, 9091–9094.

(20) Zhao, Y.; Zhang, X. B.; Han, Z. X.; Qiao, L.; Li, C. Y.; Jian, L. X.; Shen, G. L.; Yu, R. Q. *Anal. Chem.* **2009**, *81*, 7022–7030.

(21) Lee, J. W.; Jung, H. S.; Kwon, P. S.; Kim, J. W.; Bartsch, R. A.; Kim, Y.; Kim, S. J.; Kim, J. S. *Org. Lett.* **2008**, *10*, 3801–3804.

(22) Komatsu, K.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2007**, *129*, 13447–13454.

(23) Chen, X.; Nam, S. W.; Jou, M. J.; Kim, Y.; Kim, S. J.; Park, S.; Yoon, J. *Org. Lett.* **2008**, *10*, 5235–5238.

(24) Zhou, L. L.; Sun, H.; Zhang, X. H.; Wu, S. K. *Spectrochim. Acta. A* **2005**, *61*, 61–65.

(25) Zhang, X. B.; Guo, C. C.; Li, Z. Z.; Shen, G. L.; Yu, R. Q. *Anal. Chem.* **2002**, *74*, 821–825.

(26) Xu, Z.; Xiao, Y.; Qian, X.; Cui, J.; Cui, D. *Org. Lett.* **2005**, *7*, 889–892.

(27) Wu, S. P.; Huang, R. Y.; Du, K.-J. *Dalton Trans.* **2009**, 4735–4740.

(28) Luo, H. Y.; Jiang, J. H.; Zhang, X. B.; Li, C. Y.; Shen, G. L.; Yu, R. Q. *Talanta* **2007**, *72*, 575–581.

(29) Thiagarajan, V.; Ramamurthy, P.; Thirumalai, D.; Ramakrishnan, V. T. *Org. Lett.* **2005**, *7*, 657–660.

(30) Kumar, M.; Dhir, A.; Bhalla, V. *Org. Lett.* **2009**, *11*, 2567–2570.

(31) Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449–2452.

(32) Gawley, R. E.; Mao, H.; Haque, M. M.; Thorne, J. B.; Pharr, J. S. *J. Org. Chem.* **2007**, *72*, 2187–2191.

(33) Liu, B.; Yu, W.-L.; Pei, J.; Liu, S.-Y.; Lai, Y.-H.; Huang, W. *Macromolecules* **2001**, *34*, 7932–7940.

(34) Baghel, G. S.; Ramanujam, B.; Rao, C. P. *J. Photochem. Photobiol. A* **2009**, *202*, 172–177.

(35) (a) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574. (b) Tang, Y.; He, F.; Yu, M.; Feng, F.; An, L.; Sun, H.; Wang, S.; Li, Y.; Zhu, D. *Macromol. Rapid Commun.* **2006**, *27*, 389–392.

(36) Yin, J.; Guan, X. F.; Wang, D.; Liu, S. Y. *Langmuir* **2009**, *25*, 11367–11374.

(37) (a) Cao, Y. D.; Zheng, Q. Y.; Chen, C. F.; Huang, Z. T. *Tetrahedron Lett.* **2003**, *44*, 4751–4755. (b) De Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Nature* **1993**, *364*, 42–44. (c) Liu, Y.; Han, M.; Zhang, H.-Y.; Yang, L.-X.; Jiang, W. *Org. Lett.* **2008**, *10*, 2873–2876.

(d) Hanaoka, K.; Muramatsu, Y.; Urano, Y.; Terai, T.; Nagano, T. *Chem.—Eur. J.* **2010**, *16*, 568–572. (e) Mameli, M.; Aragoni, M.; Arca, M.; Caltagirone, C.; Demartin, F.; Farruggia, G.; De Filippo, G.; Devillanova, F.; Garau, A.; Isaia, F.; Lippolis, V.; Murgia, S.; Prodi, L.; Pintus, A.; Zaccheroni, N. *Chem.—Eur. J.* **2010**, *16*, 919–930. (f) Son, H.; Lee, H. Y.; Lim, J. M.; Kang, D.; Han, W. S.; Lee, S. S.; Jung, J. H. *C Chem.—Eur. J.* **2010**, *16*, 11549–11553.

(38) (a) Lee, K. W.; Wei, K. H.; Lin, H. C. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4593–4602. (b) Yang, P. J.; Wu, C. W.; Sahu, D.; Lin, H. C. *Macromolecules* **2008**, *41*, 9692–9703.

(39) Samia, A. C. S.; Cody, J.; Fahrni, C. J.; Burda, C. *J. Phys. Chem. B* **2003**, *108*, 563–569.

(40) McMillin, D. R.; McNett, K. M. *Chem. Rev.* **1998**, *98*, 1201–1220.

(41) Chen, L. X.; Jager, W. J. H.; Gosztola, D. J.; Niemczyk, M. P.; Wasielewski, M. R. *J. Phys. Chem. B* **2000**, *104*, 1950–1960.

(42) Ishizaka, S.; Wada, T.; Kitamura, N. *Photochem. Photobiol. Sci.* **2009**, *8*, 562–566.

(43) Angelici, R. J.; Allison, J. W. *Inorg. Chem.* **1971**, *10*, 2238–2243. (b) Teng, W.; Ruhlandt-Senge, K. *Chem.—Eur. J.* **2005**, *11*, 2462–2470.