



A Typical Metal-Ion-Responsive Color-Tunable Emitting Insulated π -Conjugated Polymer Film

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Abstract: We report the synthesis of an insulated π -conjugated polymer containing 2,2'-bipyridine moieties as metal coordination sites. Metal coordination to the polymer enabled easy and reversible tuning of the luminescent color without changes to the main chain skeleton. The permethylated α -cyclodextrin (PM α -CD)-based insulation structure allowed the metalated polymers to demonstrate efficient emission even in the solid state, with identical spectral shapes to the dilute solutions. In addition, the coordination ability of the metal-free polymer was maintained in the solid state, resulting in reversible changes in the luminescent color in response to the metal ions. The synthesized polymer is expected to be suitable for application in recyclable luminescent sensors to distinguish different metal ions.

Due to their superior luminescent properties and processability π -conjugated polymers (CPs) are promising materials for use in optical devices.^[1] For such applications, it must be possible to tune the luminescent colors of the polymers according to the desired practical use. In general, the luminescent colors of CPs are altered by modifying the conjugated backbones, which often involves reconstruction of the corresponding monomers. In addition, control of a polymer's luminescent colors may be possible through non-covalent bonding with external stimulating agents,^[2,3] and allows easy, direct, and reversible control of a polymer's luminescent color without changes to the main chain skeleton. In terms of external stimulating agents, metal-salts have been extensively researched due to their facile coordination with basic polymers and resulting redistribution of the electron cloud of the conjugated chains.^[4–7] It has been reported that tuning of the luminescent wavelength of π -conjugated molecules was possible by varying the metal or anionic species employed.^[5d–f,8] Application of these functions to solid-state materials is therefore expected to yield metal ion sensors. However, despite many successful examples in the solution state,^[4–7] no examples of reversible luminescent color change in neat CP films by metal ions have been reported, although stimulating agents such as protons or boranes have been shown to be effective.^[3] This is due to strong interpolymer π - π interactions causing luminescence self-quenching

in such a condensed phase.^[9] It is difficult to control such strong and random interactions in the solid state.

To suppress interpolymer π - π interactions, insulated π -conjugated polymers (ICPs) have received growing attention in recent years.^[10] ICPs possess bulky side chains or macrocycles that cover π -conjugated chains to suppress interpolymer interactions, and such systems have been reported to show efficient emission even in the solid state. For example, a high fluorescent quantum yield ($\Phi_F = 0.62$),^[11] full-color emission,^[12] and phosphorescent emission^[13e] have been reported in insulated solid-state polymers. We previously developed ICPs with polyrotaxane structures using permethylated α -cyclodextrins (PM α -CDs) as organic soluble macrocycles covalently linked to the main chains.^[13] These ICPs exhibited superior optical properties, owing to the linked rotaxane structure, thus enabling well-defined and efficient insulation. We herein report the design and synthesis of a PM α -CD-based ICP bearing 2,2'-bipyridine units as metal coordination sites (Figure 1). The PM α -CD positions are fixed by linkages to provide a size-limited cavity around the metal coordination sites. This structure allows metal ions to access the coordination sites, simultaneously preventing interactions between the metallopolymers.

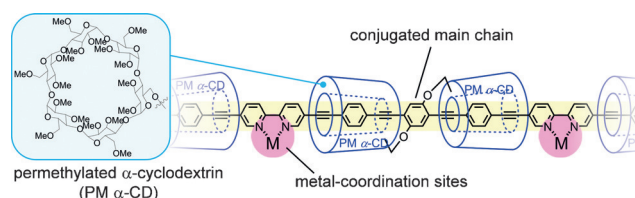
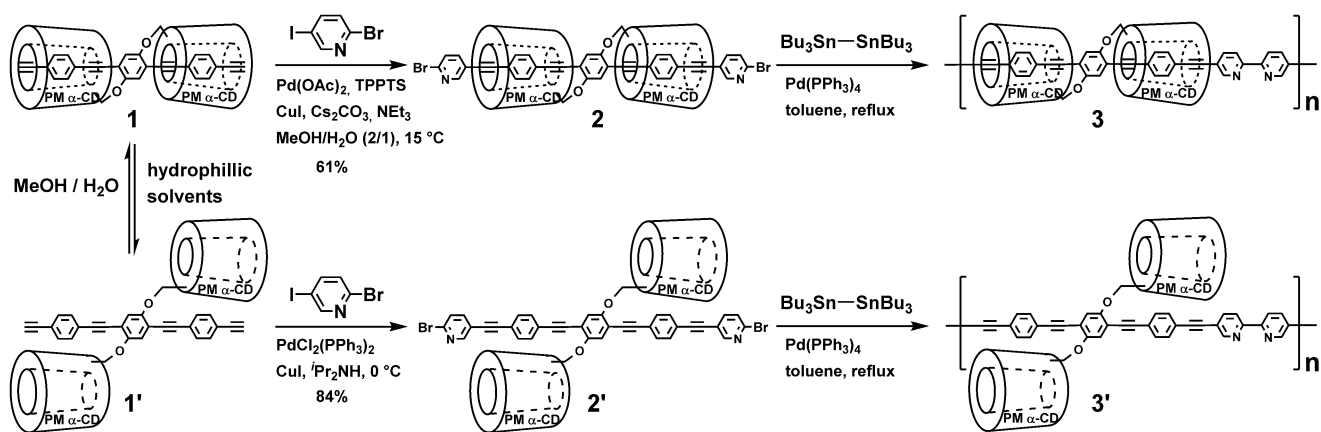


Figure 1. Design of the color-tunable ICP.

Scheme 1 shows the synthetic routes to polymer **3** and the uninsulated reference **3'**. The key step in this process is the quantitative self-inclusion of **1'**, bearing two PM α -CDs linked to the π -conjugated chain, into the insulated molecule **1**, by dissolving in a hydrophilic solvent mixture (MeOH/H₂O = 2/1).^[13b] Under the same solvent conditions, **1** was elongated via an iodo-selective Sonogashira–Hagihara cross-coupling with 2-bromo-5-iodopyridine using a water-soluble TPPTS (tris(3-sulfophenyl)phosphine trisodium salt) as the ligand in MeOH/H₂O = 2/1 (v/v) to afford **2**. Insulation of **2** was maintained under various solvent conditions as the linkage structures prevent the PM α -CDs threading out from the elongated π -conjugated chains. The insulated structure of **2** was confirmed by observing the nuclear Overhauser effect (NOE) between the inner PM α -CD protons and aryl protons in the ¹H–¹H ROESY NMR spectra (see Figure S1 in the

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Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201603160>.



Scheme 1. Synthetic routes to polymers **3** and **3'**.

Supporting Information). **2'** was selectively synthesized from precursor **1'** by simply changing solvents from a hydrophilic solvent (MeOH/H₂O) to an organic solvent (Pr₂NH). Compound **2** was then polymerized with equivalent amounts of Sn₂''Bu₆ via sequential stannylation and Migita–Kosugi–Stille cross-coupling to give polymer **3**.^[14] Insulated polymer **3** was highly soluble in a wide range of solvents (e.g., toluene, chloroform, tetrahydrofuran, acetonitrile, methanol, and *N,N*-dimethylformamide), reflecting the insulating effect of the PM α -CDs. The number average molecular weight (M_n) of insulated polymer **3** was determined to be 4.7×10^4 by size exclusion chromatography (SEC; Figure S2). Uninsulated reference **3'** was also synthesized by a similar procedure, and gave a lower M_n value (2.7×10^4) due to its lower solubility (Figure S3). The high molecular weight fractions ($M_n > 4.9 \times 10^4$) of polymers **3** and **3'** were fractionated by preparative SEC and used for optical analyses described below.

The emission properties of these polymers were compared in the various solvents and in the solid state (Table 1). Both **3** and **3'** showed blue emission with vibrational bands in CHCl₃ (Figure 2, blue line). The Stokes shift of **3** was significantly smaller than that of **3'** as the linked PM α -CDs restricted rotation of the aryl rings in phenylene-ethynylene, thus fixing their dihedral angles at a slightly twisted position.^[13d] As a result, non-radiative decay of **3** was suppressed to give a higher quantum yield ($\Phi_{PL} = 0.58$) than **3'** ($\Phi_{PL} = 0.28$) in CHCl₃. The value of λ_{PL} and Φ_{PL} of insulated **3** were much insensitive to the polarity of solvents (CHCl₃, MeCN or MeOH) than those of **3'**, reflecting the insulating effect (Figure 2). Moreover, insulated polymer **3** exhibited a con-

Table 1: Emission properties of polymer **3** and **3'**.

Solvent	3			3'		
	λ_{Abs} ^[a]	λ_{PL} ^[b]	Φ_{PL} ^[c]	λ_{Abs} ^[a]	λ_{PL} ^[b]	Φ_{PL} ^[c]
CHCl ₃	396	417, 438	0.58	408	444	0.28
90% MeCN ^d	394	416, 439	0.33	409	465	0.05
90% MeOH ^d	393	416, 438	0.25	415	475	0.09
Film	–	417, 439	0.16	–	540	0.10

[a] Unit: nm. [b] Unit: nm, excited at 380 nm. [c] Excited wavelengths were scanned at 350–400 nm. Φ_{PL} were measured using an integrating sphere.^[15] [d] 10% CHCl₃ was added to dissolve uninsulated **3'**.

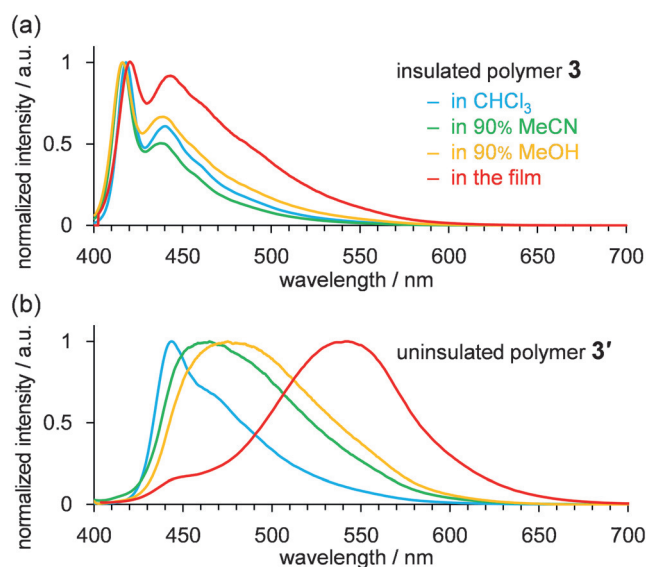


Figure 2. Emission spectra (excitation: 380 nm) of a) polymer **3** and b) **3'** in CHCl₃ (blue), 90% MeCN (green), 90% MeOH (yellow), or the solid-state film (red).

stant emission maximum even in the solid state (Figure 2a), although the relative intensity of the 0–0 transition band decreased. This clearly differed from uninsulated **3'**, where a 100 nm redshift of the emission maxima was observed (Figure 2b). The weakening of the 0–0 transition band of **3** is likely the result of the small Stokes shift (re-absorption effect), which also explains the lower Φ_{PL} values of **3** compared with metalated **3-M** in the solid state (vide infra).

π -Conjugated polymers bearing metal coordination sites (**3** and **3'**) were then coordinated with various metals (**3-M**, **3'-M**) by the addition of a range of salts (ZnCl₂, CdCl₂, GaCl₃, InCl₃, or SnCl₄), resulting in a redshift of the emission wavelength (Table 2). The degree of shifting tended to increase with an increase in valence of the metallic species. **3-M** gave comparable or greater Φ_{PL} values than those of **3**. In contrast, the Φ_{PL} value decreased for uninsulated polymer **3'** upon coordination to high-valence metals. These results demonstrate the desired adjustability of the fluorescence color for insulated polymer **3**. Previously, Ma and co-workers

Table 2: Optical properties of **3-M** and **3'-M** in CHCl₃.

Compounds		$\lambda_{\text{Abs}}/\text{nm}$	$\lambda_{\text{PL}}/\text{nm}^{[a]}$	$\Phi_{\text{PL}}^{[b]}$
3-	Zn ^{II}	405	457	0.68
	Cd ^{II}	398	451	0.58
	Ga ^{III}	410	489	0.61
	In ^{III}	404	475	0.62
	Sn ^{IV}	414	506	0.47
3'-	Zn ^{II}	423	551	0.20
	Cd ^{II}	414	506	0.32
	Ga ^{III}	438	N.D.	N.D.
	In ^{III}	426	550	0.09
	Sn ^{IV}	449, 389	N.D.	N.D.

[a] Excited at 380 nm. [b] Excited wavelengths were scanned at 350–400 nm. The Φ_{PL} values were measured using an integrating sphere.

examined the origin of the redshift of Zn^{II}-coordinated CPs.^[16] They found that Zn^{II} orbitals did not participate in any frontier orbital interactions, but that Zn^{II} acted as a positive point charge, causing a decrease in the energy level of adjacent molecular orbitals. Consequently, the lowest unoccupied molecular orbital (LUMO) localized around the bipyridine moiety and the emission took on the character of a charge-transfer transition. This calculated result agrees with our experimental result, where an increase in metal valence caused an increase in the redshift. Furthermore, the metal-induced emission redshift of polymer **3** was significantly suppressed compared to that of **3'** (Table 2). It is suggested that the insulated structure of **3** suppresses large structural changes in the excited states accompanying charge-transfer transition (the possibility that **3'** formed a 2:1 complex was eliminated by Scatchart plot; Figure S16).^[5g,17]

To gain a closer insight into the effect of metal ions, fluorescence titrations with SnCl₄ were conducted using polymer **3** (Figure 3). The relative emission intensity at each wavelength varied in a nonlinear fashion and was saturated by the addition of 0.5 equiv. of SnCl₄. This differed from the absorption trace of the excited wavelength (380 nm), which showed a much more gradual decrease upon the addition of up to 1.0 equiv. SnCl₄ (Figure S14). This behavior suggests that energy transfer from metal-free chromophores to meta-

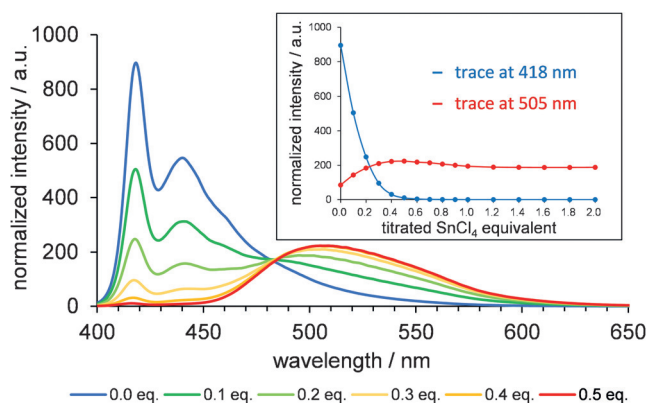


Figure 3. Changes in the emission spectra of polymer **3** upon SnCl₄ titration (excitation: 380 nm). The inset indicates emission intensity traces at 418 nm (derived from the metal-free chromophore) and 505 nm (derived from the Sn^{IV}-coordinated chromophore).

lated chromophores took place. This sensitivity renders the CPs particularly suitable for use in metal-sensing applications.^[18]

The **3-M** films were then fabricated by casting their CHCl₃ solutions on SiO₂ substrates. As stated above, π -conjugated polymers generally show significant fluorescence spectral changes and decreased emission efficiency upon film formation.^[9] However, **3-M** exhibited strong emission even in the solid state. The emission spectra of the films (Figure 4, solid lines) were comparable to those of dilute solutions (Figure 4,

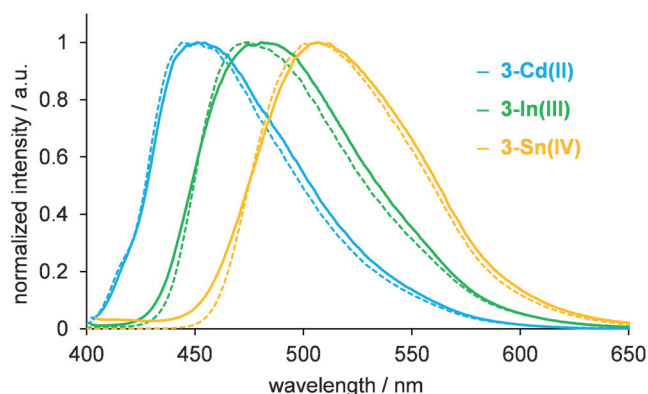


Figure 4. Emission spectra (excitation: 380 nm) of **3-Cd**^{II} (light blue), **3-In**^{III} (green), and **3-Sn**^{IV} (yellow). Dashed lines indicate spectra measured in CHCl₃. Solid lines indicate spectra measured from solid state films.

dashed line), with the exception of **3-Zn**^{II}, which showed a redshift of about 20 nm from the solution value (Table 3). Furthermore, insulated metallopolymer **3-M** maintained efficient emission ($\Phi_{\text{PL}} = 0.16$ – 0.46 ; Table 3) in contrast to the corresponding uninsulated metallopolymer **3'-M** ($\Phi_{\text{PL}} < 0.19$, Figure S9). In particular, the quantum yield of **3-Sn**^{IV} ($\Phi_{\text{PL}} = 0.46$) was significantly high among conjugated metallopolymer films. These results demonstrate the superior insulating ability of the PM α -CD-based linked rotaxane structure, as generally, the suppression of interactions between π -conjugated metallopolymer (including ionic interactions and π - π interactions) is challenging.

Finally, the coordination ability and reversibility of the metal-free polymer film **3** were examined. The blue-emitting film of **3** (Figure 5A) was dipped into a Et₂O solution containing 0.3 mM SnCl₄ at room temperature for 5 s. The emission color of the dipped moieties immediately changed into the representative colors for SnCl₄ (Figure 5B), and the emission spectra of the dipped regions were identical to those of the films formed by casting **3-Sn**^{IV} solution (Figure S10). The larger area of the film was subsequently dipped into

Table 3: Emission properties of polymer **3-M** in the solid state.

3-	Zn ^{II}	Cd ^{II}	Ga ^{III}	In ^{III}	Sn ^{IV}
$\lambda_{\text{PL}}/\text{nm}$	477	451	486	480	507
$\Phi_{\text{PL}}^{[a]}$	0.35	0.16	0.31	0.39	0.46

[a] Excited wavelengths were scanned at 350–400 nm. Φ_{PL} were measured using an integrating sphere.

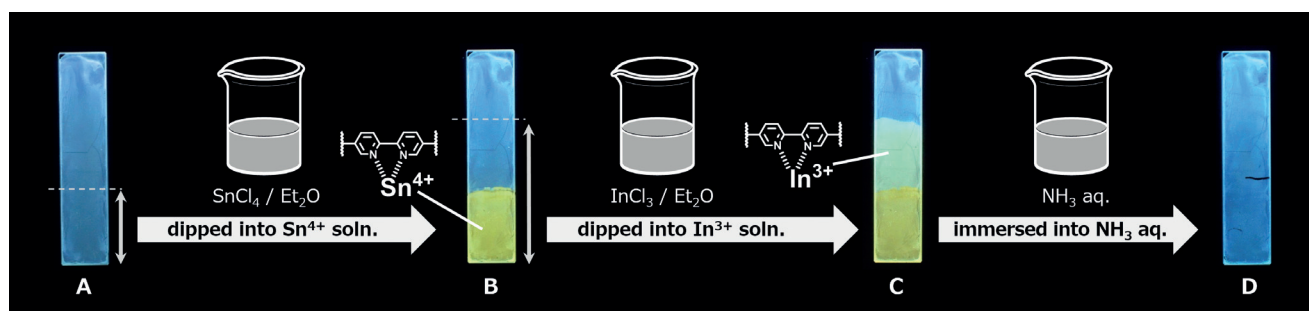


Figure 5. Change in emission color of polymer **3** film with exposure to metal ions. Photographic images were taken under UV irradiation at 365 nm. Double-headed arrows indicate the dipped regions of the films. These steps were conducted in order A-B-C-D.

a 3 mM InCl_3 Et_2O solution for 20 s, and the non-metalated region changed into the representative colors for InCl_3 (Figure 5C). Interestingly, the Sn^{IV} -coordinated region did not exhibit a luminescent color change upon contact with the In^{III} solution due to the strong Sn^{IV} coordination. Furthermore, the above luminescent color changes were easily erased through removal of the coordinated metals by immersion in an aqueous NH_3 solution (Figure 5D). The recycled film exhibited the original blue emission, and once again demonstrated a coordination ability to the various metals, thus confirming the reversibility of this process. This polymer is therefore expected to be applicable in recyclable sensor materials to distinguish metal ions. The ICP synthesized in this work is an example of a novel polymer design, which enables metallopolymers to extend their unique properties to solid-state materials.

Acknowledgements

This research was supported by JSPS KAKENHI grant numbers JP16H00834, JP16H00965, and JP26288090. This research was also supported by Tokuyama Science Foundation and CREST, JST.

Keywords: cyclodextrins · fluorescence · luminescence · polymers · supramolecular chemistry

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 13427–13431
Angew. Chem. **2016**, *128*, 13625–13629

- [1] a) A. Ajayaghosh, *Chem. Soc. Rev.* **2003**, *32*, 181; b) I. F. Perepichka, D. F. Perepichka, H. Meng, F. Wudl, *Adv. Mater.* **2005**, *17*, 2281; c) A. Facchetti, *Chem. Mater.* **2011**, *23*, 733; d) M. S. AlSalhi, J. A. Lawrence, A. Dass, M. Raja, *Int. J. Mol. Sci.* **2011**, *12*, 2036.
- [2] a) S. Kappaun, S. Horner, A. M. Kelterer, K. Waich, F. Grasse, M. Graf, L. Romaner, F. Niedermair, K. Mullen, A. C. Grimsdale, R. Saf, E. J. List, E. Zojer, C. Slugovc, *Macromol. Chem. Phys.* **2008**, *209*, 2122; b) G. C. Welch, G. C. Bazan, *J. Am. Chem. Soc.* **2011**, *133*, 4632; c) P. Zalar, B. Henson, G. C. Welch, G. C. Bazan, T. Nguyen, *Angew. Chem. Int. Ed.* **2012**, *51*, 7495; *Angew. Chem.* **2012**, *124*, 7613; d) D. Tanaka, J. Ohshita, Y. Ooyama, Y. Morihara, *Polym. J.* **2013**, *45*, 1153.
- [3] a) S. Hayashi, A. Asano, T. Koizumi, *Polym. Chem.* **2011**, *2*, 2764; b) S. Hayashi, A. Asano, T. Koizumi, *RSC Adv.* **2013**, *3*, 7375; c) S. Hayashi, T. Koizumi, *J. Polym. Sci. Part A* **2014**, *52*, 3142.
- [4] As for ether-type ligands; a) M. J. Marsella, T. M. Swager, *J. Am. Chem. Soc.* **1993**, *115*, 12214; b) M. J. Marsella, R. J. Newland, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1995**, *117*, 9842.
- [5] As for bipyridine or phenanthroline-type ligands; a) B. Wang, M. R. Wasielewski, *J. Am. Chem. Soc.* **1997**, *119*, 12; b) L. X. Chen, W. J. H. Jaeger, D. J. Gosztola, M. P. Niemczyk, M. R. Wasielewski, *J. Phys. Chem. B* **2000**, *104*, 1950; c) B. Liu, W. L. Yu, J. Pei, S. Y. Liu, Y. H. Lai, W. Huang, *Macromolecules* **2001**, *34*, 7932; d) T. Yasuda, T. Yamamoto, *Macromolecules* **2003**, *36*, 7513; e) T. Yasuda, I. Yamaguchi, T. Yamamoto, *Adv. Mater.* **2003**, *15*, 8503, 293; f) L. Tian, W. Zhang, B. Yang, P. Lu, M. Zhang, D. Lu, Y. Ma, J. Shen, *J. Phys. Chem. B* **2005**, *109*, 6944; g) A. Kokil, P. Yao, C. Weder, *Macromolecules* **2005**, *38*, 3800; h) Y. Kim, J. K. Lee, W. H. Park, T. S. Lee, *Thin Solid Films* **2005**, *477*, 100; i) S. He, S. T. Iacono, S. M. Budy, A. E. Dennis, D. W. Smith, R. C. Smith, *J. Mater. Chem.* **2008**, *18*, 1970; j) S. He, A. E. Dennis, R. C. Smith, *Macromol. Rapid Commun.* **2009**, *30*, 2079; k) S. He, A. A. Buel, J. M. Hanley, B. P. Morgan, A. G. Tennyson, R. C. Smith, *Macromolecules* **2012**, *45*, 6344; l) D. A. Turchetti, P. C. Rodrigues, L. S. Berlim, C. Zanlorenzi, G. C. Faria, T. D. Z. Atvars, W. H. Schreiner, L. C. Akcelrud, *Synth. Met.* **2012**, *162*, 35.
- [6] As for terpyridine-type ligands; a) M. Kimura, T. Horai, K. Hanabusa, H. Shirai, *Adv. Mater.* **1998**, *10*, 459; b) Q. Chu, Y. Pang, *J. Polym. Sci. Part A* **2006**, *44*, 2338; c) V. Banjoko, Y. Xu, E. Mintz, Y. Pang, *Polymer* **2009**, *50*, 2001; d) A. R. Rabindranath, A. Maier, M. Schäfer, B. Tieke, *Macromol. Chem. Phys.* **2009**, *210*, 659.
- [7] As for other types of ligands; a) Y. Xu, J. Meng, L. Meng, Y. Dong, Y. Cheng, C. Zhu, *Chem. Eur. J.* **2010**, *16*, 12898; b) N. Y. Kwon, D. Kim, J. H. Son, G. S. Jang, J. H. Lee, T. S. Lee, *Macromol. Rapid Commun.* **2011**, *32*, 1061; c) K. Seehafer, M. Bender, U. H. F. Bunz, *Macromolecules* **2014**, *47*, 922; d) I. Yamaguchi, T. Nagano, *J. Appl. Polym. Sci.* **2014**, *131*, 1; e) F. Li, F. Meng, Y. Wang, C. Zhu, Y. Cheng, *Tetrahedron* **2015**, *71*, 1700.
- [8] a) K. P. Divya, S. Savithri, A. Ajayaghosh, *Chem. Commun.* **2014**, *50*, 6020; b) S. M. Brombosz, A. J. Zuccherro, R. L. Phillips, D. Vazquez, A. Wilson, U. H. F. Bunz, *Org. Lett.* **2007**, *9*, 4519.
- [9] Detailed studies on aggregation effects of CPs; a) I. D. W. Samuel, G. Rumbles, C. Collison, *J. Phys. Rev. B* **1995**, *52*, R11573; b) D. Oelkrag, H.-J. Egelhaaf, J. Gierschner, A. Tompert, *Synth. Met.* **1996**, *76*, 249; c) E. Tekin, H. Wijlaars, E. Holder, D. A. M. Egbe, U. S. Schubert, *J. Mater. Chem.* **2006**, *16*, 4294; d) D. Sahoo, K. Sugiyasu, Y. Tian, M. Takeuchi, I. G. Scheblykin, *Chem. Mater.* **2014**, *26*, 4867.
- [10] a) M. J. Frampton, H. L. Anderson, *Angew. Chem. Int. Ed.* **2007**, *46*, 1028; *Angew. Chem.* **2007**, *119*, 1046; b) J. Terao, *Polym. Chem.* **2011**, *2*, 2444; c) J. Terao, *Chem. Rec.* **2011**, *11*, 269; d) C. Pan, C. Zhao, M. Takeuchi, K. Sugiyasu, *Chem. Asian J.* **2015**, *10*,

- 1820; e) H. Masai, J. Terao, T. Yasushi, *Tetrahedron Lett.* **2014**, 55, 4035.
- [11] C. H. Zhao, A. Wakamiya, S. Yamaguchi, *Macromolecules* **2007**, 40, 3898.
- [12] C. Pan, K. Sugiyasu, Y. Wakayama, A. Sato, M. Takeuchi, *Angew. Chem. Int. Ed.* **2013**, 52, 10775; *Angew. Chem.* **2013**, 125, 10975.
- [13] a) J. Terao, S. Tsuda, Y. Tanaka, K. Okoshi, T. Fujihara, Y. Tsuji, N. Kambe, *J. Am. Chem. Soc.* **2009**, 131, 16004; b) J. Terao, Y. Tanaka, S. Tsuda, N. Kambe, M. Taniguchi, T. Kawai, A. Saeki, S. Seki, *J. Am. Chem. Soc.* **2009**, 131, 18046; c) J. Terao, A. Wadahama, A. Matono, T. Tada, S. Watanabe, S. Seki, T. Fujihara, Y. Tsuji, *Nat. Commun.* **2013**, 4, 1691; d) H. Masai, J. Terao, S. Seki, S. Nakashima, M. Kiguchi, K. Okoshi, T. Fujihara, Y. Tsuji, *J. Am. Chem. Soc.* **2014**, 136, 1742; e) H. Masai, J. Terao, S. Makuta, T. Tachibana, T. Fujihara, Y. Tsuji, *J. Am. Chem. Soc.* **2014**, 136, 14714.
- [14] P. F. H. Schwab, F. Fleischer, J. Michl, *J. Org. Chem.* **2002**, 67, 443.
- [15] N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, R. H. Friend, *Chem. Phys. Lett.* **1995**, 241, 89.
- [16] B. Yang, L. Tian, H. Zhang, W. Zhang, H. Xu, Z. Xie, P. Lu, M. Zhang, J. Yu, D. Lu, Y. Ma, J. Shen, X. Liu, *J. Phys. Chem. B* **2006**, 110, 16846.
- [17] G. Scatchard, *Ann. N. Y. Acad. Sci.* **1949**, 51, 660.
- [18] a) S. W. Thomas, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, 107, 1339; b) S. Rochat, T. M. Swager, *ACS Appl. Mater. Interfaces* **2013**, 5, 4488; c) U. H. F. Bunz, K. Seehafer, M. Bender, M. Porz, *Chem. Soc. Rev.* **2015**, 44, 4322.

Received: March 31, 2016

Revised: June 16, 2016

Published online: July 7, 2016