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Phosphole- and Benzodithiophene-Based Copolymers: Synthesis and Application in Organic Photovoltaics

CLUSTER ISSUE

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Two kinds of phosphole- and benzodithiophene-based copolymers bearing P^V=O or $P^V=NSO_2C_8H_{17}$ functions were prepared by Pd–CuI-promoted Stille coupling reactions, and their optical and electrochemical properties were investigated. Bulk heterojunction organic photovoltaic devices comprised of the new P,S-bridged copolymers and (6,6)-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) exhibited power conversion efficiencies of up to 0.65 % under AM1.5 irradiation at 100 mW cm^{-2}.

Introduction

Recent progress in the field of bulk heterojunction organic photovoltaics (OPV) has encouraged many chemists to construct a new class of low-bandgap conjugated copolymers that absorb light at a longer wavelength.[1] In particular, donor–acceptor (D–A)-type copolymers containing electron-rich thiophene derivatives and electron-deficient heterocyclopentadienes (heteroles) have been frequently used as the sensitizers, because alternating D–A subunits intrinsically lower the optical bandgap owing to the charge-transfer (CT) character. For instance, OPV devices fabricated with benzo[1,2-*b*:4,5-*b′*]dithiophene-based D–A copolymers (e.g., PBDTTPD[2] and PBDTTT[3]) and fullerene derivatives were reported to show high power conversion efficiencies (PCE) of up to 7.6%. An important subject in the molecular design of D–A copolymers is the development of electronically tunable acceptor subunits with high electron affinity.

The LUMO level of phosphole is influenced, among other things, by stabilizing hyperconjugative interactions, and can be lowered significantly further by variation of the phosphorus substituent.[4] In this regard, thiophene–phosphole-based D–A-type copolymers, in which the phosphole acts as an electron-accepting unit, are potential low-bandgap sensitizers for use in OPV. To date, several kinds of phosphole-containing π-conjugated copolymers have been reported.[5–10] For example, Réau et al.[6] and Baumgartner et al.[7] prepared phosphole–thiophene- and dithieno[*b*,*d*]phosphole–carbazole-based copolymers, **P1** and **P2**, respectively (Figure 1), and studied their electronic and fluorescent properties in detail. To the best of our knowledge, however, no attempt has been made to use thiophene–phosphole-based D–A copolymers in OPV devices.

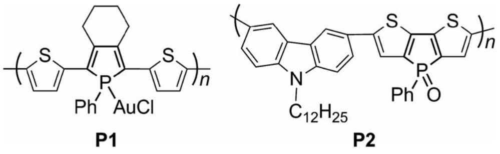

Figure 1. Previous examples of thiophene–phosphole-based copolymers **P1** and **P2**.[6,7]

Recently, we reported the first examples of poly(phosphole *P*-oxide)[11] and poly(phosphole *P*-imide)s,[12] both of which were successfully prepared by using Stille coupling reactions of the corresponding phosphole monomers. In addition, these polyphospholes were found to possess narrow HOMO–LUMO gaps and ambipolar charge-carrier transport properties derived from the polarizable nature of the phosphorus-bridged diene units. Herein, we report the first examples of phosphole–benzodithiophene (BDT)-based conjugated copolymers bearing P^V=O or $P^V=NSO_2C_8H_{17}$ functions. The optical and electrochemical properties of the newly synthesized D–A copolymers and their application in OPV devices have been investigated.

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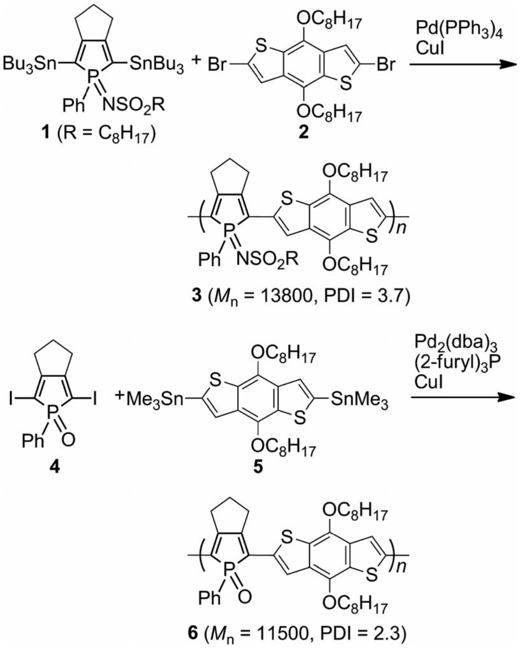
Results and Discussion

Scheme 1 summarizes the syntheses of phosphole–BDT-based copolymers **3** and **6**, which involve Stille coupling reactions between (i) 2,5-bis(tributylstannyl)phosphole *P*-imide (**1**)[12] and 2,6-dibromobenzo[1,2-*b*:4,5-*b′*]dithiophene (**2**)[13] or (ii) 2,5-diiodophosphole *P*-oxide (**4**)[11] and 2,6-bis(trimethylstannyl)benzo[1,2-*b*:4,5-*b′*]dithiophene (**5**).[14] In both reactions, the addition of CuI was indispensable to smoothly promote the cross-coupling, namely, polymerization. Copolymers **3** and **6** were isolated as bluish-violet solids by repeated reprecipitation from CH_2Cl_2/MeOH and CH_2Cl_2/hexane. The number-average molecular weight (M_n) and the polydispersity index (PDI) of the polymers were determined by gel permeation chromatography (vs. polystyrene standards). The ^{31}P NMR spectra of **3** and **6** in CD_2Cl_2 displayed broad peaks at δ = 35 and 52 ppm, respectively.



Scheme 1. Synthesis of copolymers **3** and **6**.

The UV/Vis/NIR absorption spectra of **3** and **6** are shown in Figure 2. In CH_2Cl_2, the absorption maximum (λ_{max}) and onset (λ_{onset}) of **3** are somewhat redshifted relative to those of **6**, which suggests that the P^V substituents affect the electronic transition energies of the copolymer π networks (Table 1). In the film state, however, the reverse relationship was observed. The λ_{max} and λ_{onset} values of **6** are redshifted relative to those of **3**. This may be attributable to the differences in the intermolecular π–π interaction and configuration of the polymer chains in the solid state. Presumably, the less bulky P=O groups in **6** reduce the spatial separation of the polymer networks more than the $P=NSO_2C_8H_{17}$ groups in **3** (see below). The optical HOMO–LUMO gaps of **3** and **6** determined from their λ_{onset} values in films are 1.73 and 1.69 eV, respectively. The ionization potentials of **3** and **6** were also determined by photoemission yield spectroscopy of the thin films (Figure S1 in Supporting Information). The observed values of 5.65 (**3**) and 5.32 eV (**6**) are comparable to those of PBDTTPD (5.4–5.57 eV),[2] which suggests that the incorporation of the phosphole subunits is effective for lowering the HOMO levels of the D–A copolymers. The LUMO levels of **3** and **6** were calculated to be 3.92 and 3.63 eV, respectively, from the observed ionization potentials and the optical HOMO–LUMO gaps.

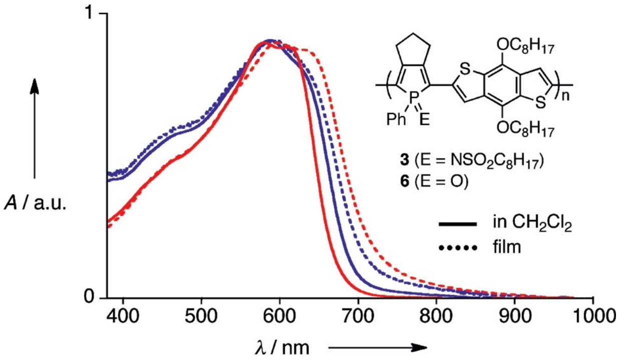


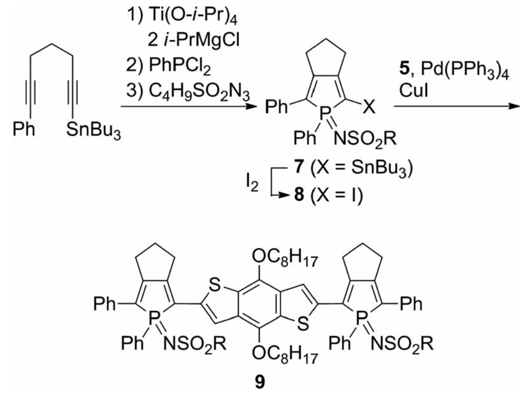
Figure 2. Normalized UV/Vis/NIR absorption spectra of **3** (blue) and **6** (red).

Table 1. Optical and electrochemical data for **3** and **6**.

	λ_{max} [nm]	λ_{onset} [nm]	HOMO [eV][a]	LUMO [eV][b]
3 (soln)	588	710	n.d.	n.d.
3 (film)	590	715	5.65	3.92
6 (soln)	579	690	n.d.	n.d.
6 (film)	596	735	5.32	3.63

[a] Determined by photoemission yield spectroscopy. [b] Determined from HOMO levels and optical HOMO–LUMO gaps. n.d. = not determined.

To attain some insight into the fundamental properties of the present A–D–A fragment, the phosphole–BDT–phosphole derivative **9** was newly prepared (Scheme 2). 2-Tributylstannyl-5-phenylphosphole *P*-imide (**7**), prepared from 1-tributylstannyl-7-phenyl-1,6-heptadiyne,[11] was treated with iodine to give 2-iodo-5-phenylphosphole *P*-imide (**8**). A Stille coupling reaction between **8** and **5** in the presence of CuI afforded one of the diastereomers of **9** (δ_P = 37.0 ppm) as a blood-red solid after column chromatography.



Scheme 2. Synthesis of **9** (R = C_4H_9).

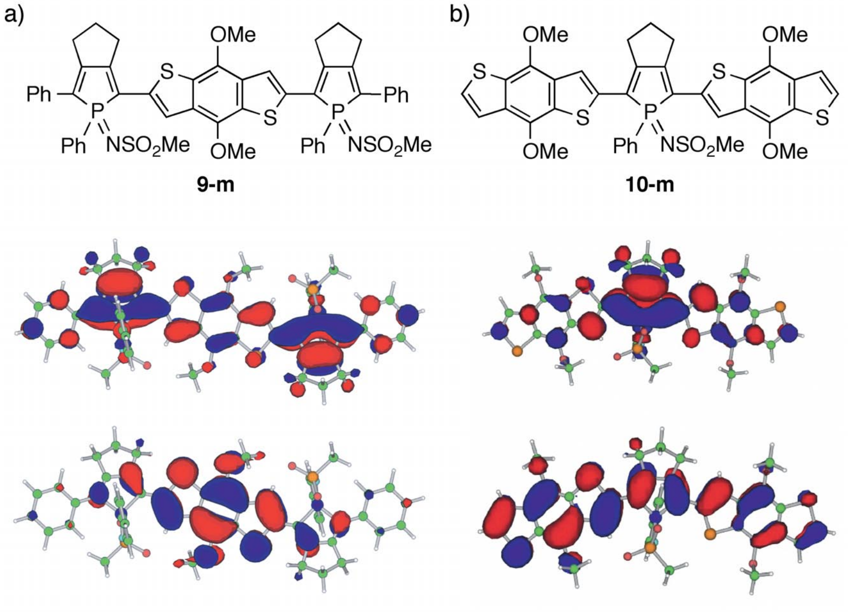


Figure 3. HOMO (lower) and LUMO (upper) diagrams of (a) *anti*-**9-m** and (b) **10-m**.

Compound **9** displayed absorption and emission maxima at 509 and 663 nm, respectively (see Figure S2 in the Supporting Information). The relatively large Stokes shift of 4560 cm^{-1} indicates the high intramolecular CT character in the excited state of **9**. Indeed, the density functional theory calculations of A–D–A model **9-m** and D–A–D model **10-m** support this interpretation; the HOMO is rather localized on the BDT moieties, whereas the LUMO is localized on the phosphole moieties (Figure 3). There are slight differences in the HOMO and LUMO energies between the two diastereomers of **9-m** (Figure S3 in the Supporting Information), which implies that the stereochemistry at the phosphorus(V) centers does not significantly affect the electronic properties of the A–D–A fragment.[15] The oxidation and reduction potentials of **9** were determined to be +0.49 and –1.65 V (vs. Fc/Fc$^+$), respectively, by cyclic voltammetry. The energy gap of 2.14 V is close to the optical HOMO–LUMO gap (2.12 eV) determined from the λ_{ab} and λ_{em} values.

With the new D–A copolymers **3** (PPNBDT) and **6** (PPOBDT) in hand, we investigated their photovoltaic properties using bulk heterojunction OPV devices with a device structure of indium tin oxide (ITO)/poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS)/PPXBDT:PC$_{71}$BM/Al (see Figures S4 and S5 in the Supporting Information). The active layer was spin-coated from chlorobenzene solutions onto the hole transport layer (PEDOT:PSS). Both **3** and **6** are stable over 300 °C (T_{d10} = 325 °C for **3** and 335 °C for **6**). The current–voltage characteristics of the OPV devices under simulated AM 1.5G solar irradiation at 100 mW cm^{-2} are illustrated in Figure 4 together with the open-circuit voltages (V_{OC}), short-circuit current densities (J_{SC}), fill factors (FF), and PCE values. It should be noted that V_{OC}, J_{SC}, FF, and PCE of the PPOBDT-based device are higher than those of the PPNBDT-based device. Presumably, the PPOBDT π network is more densely packed (see above) and transports the charge carriers more effectively than the PPNBDT π network. The preliminary PCE value of 0.65% as well as the other parameters (V_{OC} and J_{SC}) is still low compared to the previously reported PCE values for OPV devices with BDT-based D–A copolymers.[2,3] Nevertheless, the present results demonstrate for the first time that the phosphole subunits can behave as key components in the D–A copolymers for OPV.

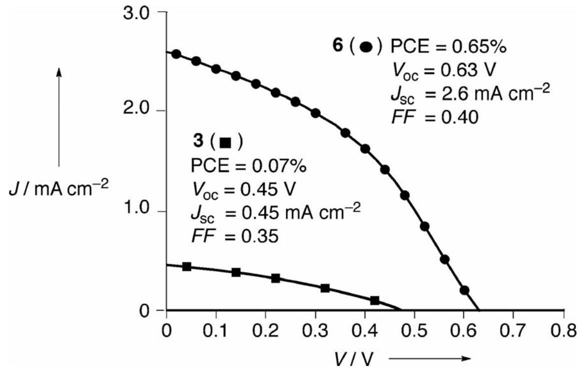


Figure 4. Current–voltage curves of the OPV devices comprised of **3** (squares) and **6** (circles).

Conclusion

We have prepared the first examples of phosphole–BDT-based conjugated copolymers by using CuI-promoted Stille coupling reactions. These D–A copolymers were found to absorb a wide range of visible light reaching 735 nm, which is attributable to the intramolecular CT between the two different heterole components. We also fabricated bulk heterojunction OPV devices containing the phosphole–BDT-based copolymers and $PC_{71}BM$, and evaluated their device performances. The PCE and J_{sc} values were found to differ significantly depending on the P=E functions (E = O, $NSO_2C_8H_{17}$). This may imply that the P^V substituents make a large impact on the charge-generation efficiency and/or charge-carrier pathways in the blend films. To achieve the higher PCE values, the synthesis of a new series of phosphole-containing D–A-type materials based on the more sophisticated molecular design is now in progress.

Experimental Section

Synthesis of Polymer 3: A mixture of **1** (242 mg, 0.25 mmol), **2** (151 mg, 0.25 mmol), $[Pd(PPh_3)_4]$ (5.0 mg, 0.0043 mmol), CuI (47.4 mg, 0.25 mmol), and toluene (13 mL) was heated at 110 °C. After 25.5 h at this temperature, iodobenzene (1.4 µL, 0.013 mmol) was added to the mixture, which was then cooled down to room temperature. The addition of methanol (300 mL) caused the precipitation of a polymer, which was collected by filtration. The polymer was purified by repeated reprecipitation from CH_2Cl_2/MeOH and CH_2Cl_2/hexane and by treatment with metal scavengers. Finally, **3** was isolated as a dark bluish-violet solid (143 mg, 68 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.65–1.22 (m), 1.36 (br. s), 1.45–1.95 (m), 2.45 (br. s), 2.80–3.40 (m), 3.95–4.35 (m), 7.10–7.20 (m), 7.35–7.74 (m), 7.78–8.10 (m) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta \approx 35$ ppm. IR (ATR): $\tilde{\nu}_{max}$ 1262 (P=N) cm^{-1}.

Synthesis of Polymer 6: A mixture of **4** (119 mg, 0.25 mmol), **5** (198 mg, 0.25 mmol), $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone; 23 mg, 0.025 mmol), $(2\text{-furyl})_3P$ (12 mg, 0.05 mmol), CuI (114 mg, 0.6 mmol), and *N*-methyl-2-pyrrolidone (NMP; 6.0 mL) was stirred at room temperature. After 100 h, iodobenzene (3 µL, 0.025 mmol) was added, and the mixture was stirred for a further 1 h. The resulting mixture was poured into MeOH (300 mL) and the precipitates were collected. The polymer was purified by repeated reprecipitation (CH_2Cl_2/MeOH/CH_2Cl_2 = 2:1) and by treatment with metal scavengers (MPA). Finally, **6** was isolated as a dark blue solid (103 mg, 62 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.93 (br. s), 1.26–1.67 (m), 1.70–2.05 (m), 2.15–3.72 (m), 2.95–3.20 (m), 4.05–4.15 (m), 7.26–7.61 (m), 7.73–7.95 (m) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 52 (br. s) ppm. IR (ATR): $\tilde{\nu}_{max}$ = 1173 (P=O) cm^{-1}.

Fabrication and Characterization of Polymer Solar Cells: Indium tin oxide (ITO) on a glass substrate with a sheet resistance of $5\,\Omega\,sq^{-1}$ (Geomatec) was used. The substrates were sonicated consecutively with acetone and ethanol for 15 min. After blow drying and UV/ozone treatment, the substrates were spin coated at 1000 rpm with poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS, Clevios P VP AI 4083) and dried in an oven at 200 °C for 10 min. For the fabrication of the active layer with bulk heterojunction structure, a mixed solution of polymer ($7.2\,mg\,mL^{-1}$) and $PC_{71}BM$ ($14.4\,mg\,mL^{-1}$) in chlorobenzene was spin-coated at 1000 rpm for 1 min onto the ITO/PEDOT:PSS under an argon atmosphere. Finally, an Al (Kojundo Chemical Lab. Co.) layer was deposited by thermal evaporation under vacuum (5×10^{-5} Pa) to yield the layered device structure (denoted as ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Al). Schematic illustrations of the top and side views of the device are depicted in Figure S5 in the Supporting Information. Photocurrent–voltage characteristics were measured under an argon atmosphere and simulated solar light ($100\,mW\,cm^{-2}$, AM1.5). Photocurrent–voltage characteristics were measured by 2400 SourceMeter (Keithley) with OTENTO-SUN III solar simulator (Bunkoukeiki).

Supporting Information (see footnote on the first page of this article): Experimental details, DFT calculation results, and spectroscopic data are presented.

Acknowledgments

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[1] For example, see: a) B. C. Thompson, J. M. J. Fréchet, *Angew. Chem.* **2008**, *120*, 62; *Angew. Chem. Int. Ed.* **2008**, *47*, 58; b) *Handbook of Thiophene-Based Materials; Applications in Organic Electronics and Photonics* (Eds.: I. F. Perepichka, D. F. Perepichka), Wiley, West Sussex, **2009**; c) F. S. Kim, G. Ren, S. A. Jenekhe, *Chem. Mater.* **2011**, *23*, 682, and references therein.

[2] BDTTPD = benzo[1,2-*b*:4,5-*b′*]dithiophene–thieno[3,4-*c*]pyrrole-4,6-dione hybrid. See, for example: a) Y. Zou, A. Najari, P. Berrouard, S. Beaupré, B. R. Aïch, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.* **2010**, *132*, 5330; b) C. Piliego, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2010**, *132*, 7595.

[3] BDTTT = benzo[1,2-*b*:4,5-*b′*]dithiophene–thieno[3,4-*b*]thiophene hybrid. See, for example: a) H. Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Tu, Y. Wu, G. Li, *Nat. Photonics* **2009**, *3*, 649; b) L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li, J. Hou, *Angew. Chem.* **2011**, *123*, 9871; *Angew. Chem. Int. Ed.* **2011**, *50*, 9697.

[4] For example, see: a) F. Mathey, *Angew. Chem.* **2003**, *115*, 1616; *Angew. Chem. Int. Ed.* **2003**, *42*, 1578; b) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1; c) L. D. Quin, *Curr. Org. Chem.* **2006**, *10*, 43; d) T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681; Correction: **2007**, *107*, 303; e) R. Réau, P. W. Dyer, in *Comprehensive Heterocyclic Chemistry III* (Eds.: C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor), Elsvier, Oxford, **2008**, chapter 3.15, pp. 1029–1048; f) Y. Matano, H. Imahori, *Org. Biomol. Chem.* **2009**, *7*, 1258; g) Y. Ren, T. Baumgartner, *Dalton Trans.* **2012**, *41*, 7792; h) L. Nyulászi, Z. Benkő, *Top. Heterocycl. Chem.* **2009**, *19*, 27.

[5] a) S. S. H. Mao, T. D. Tilley, *Macromolecules* **1997**, *30*, 5566; b) B. L. Lucht, S. S. H. Mao, T. D. Tilley, *J. Am. Chem. Soc.* **1998**, *120*, 4354.

[6] a) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi, R. Réau, *Chem. Eur. J.* **2001**, *7*, 4222; b) M. Sebastian, M. Hissler, C. Fave, J. Rault-Berthelot, C. Odin, R. Réau, *Angew. Chem.* **2006**, *118*, 6298; *Angew. Chem. Int. Ed.* **2006**, *45*, 6152; c) V. L. de Talancé, M. Hissler, L.-Z. Zhang, T. Kárpáti, L. Nyulászi, D. Caras-Quintero, P. Bäuerle, R. Réau, *Chem. Commun.* **2008**, 2200.

[7] a) T. Baumgartner, W. Bergmans, T. Kárpáti, T. Neumann, M. Nieger, L. Nyulászi, *Chem. Eur. J.* **2005**, *11*, 4687; b) S. Durben, Y. Dienes, T. Baumgartner, *Org. Lett.* **2006**, *8*, 5893; c) R. A. Krüger, T. J. Gordon, T. C. Sutherland, T. Baumgartner, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1201; d) M. Stolar, T. Baumgartner, *New J. Chem.* **2012**, *36*, 1153.

[8] a) Y. Makioka, T. Hayashi, M. Tanaka, *Chem. Lett.* **2004**, *33*, 44; b) Z. Zhang, J. Li, B. Huang, J. Qin, *Chem. Lett.* **2006**, *35*, 958; c) R.-F. Chen, R. Zhu, Q.-L. Fan, W. Huang, *Org. Lett.* **2008**, *10*, 2913.

[9] a) Y. Morisaki, Y. Aiki, Y. Chujo, *Macromolecules* **2003**, *36*, 2594; b) H.-S. Na, Y. Morisaki, Y. Aiki, Y. Chujo, *Polym. Bull.*

2007, *45*, 645; c) H.-S. Na, Y. Morisaki, Y. Aiki, Y. Chujo, *J. Polym. Sci. Part A*, *Polym. Chem.* **2007**, *45*, 2867; d) Y. Morisaki, H.-S. Na, Y. Aiki, Y. Chujo, *Polym. Bull.* **2007**, *58*, 777.

[10] a) I. Tomita, M. Ueda, *Macromol. Symp.* **2004**, *209*, 217; b) I. Tomita, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **2004**, *45*, 415.

[11] A. Saito, Y. Matano, H. Imahori, *Org. Lett.* **2010**, *12*, 2675.

[12] Y. Matano, H. Ohkubo, Y. Honsho, A. Saito, S. Seki, H. Imahori, *Org. Lett.* **2013**, *15*, 932.

[13] S. A. Jenekhe, S. Subramaniyan, E. Ahmed, H. Xin, F. S. Kim, WO2011051292 (A1), **2011**.

[14] Y. Liang, U. Wu, D. Femg, S.-T. Tsai, H.-J. Son, G. Li, L. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 56.

[15] A similar result was observed for two diastereomers of 2,2′-bis(benzo[*b*]phosphole) *P*-oxides; there is little difference in the absorption/emission maxima and the redox potentials between them. Y. Hayashi, Y. Matano, K. Suda, Y. Kimura, Y. Nakao, H. Imahori, *Chem. Eur. J.* **2012**, *18*, 15972.

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