

Supporting Information

**Synthesis of new conjugated polymers with coordinated praseodymium
complex for polymer memory devices**

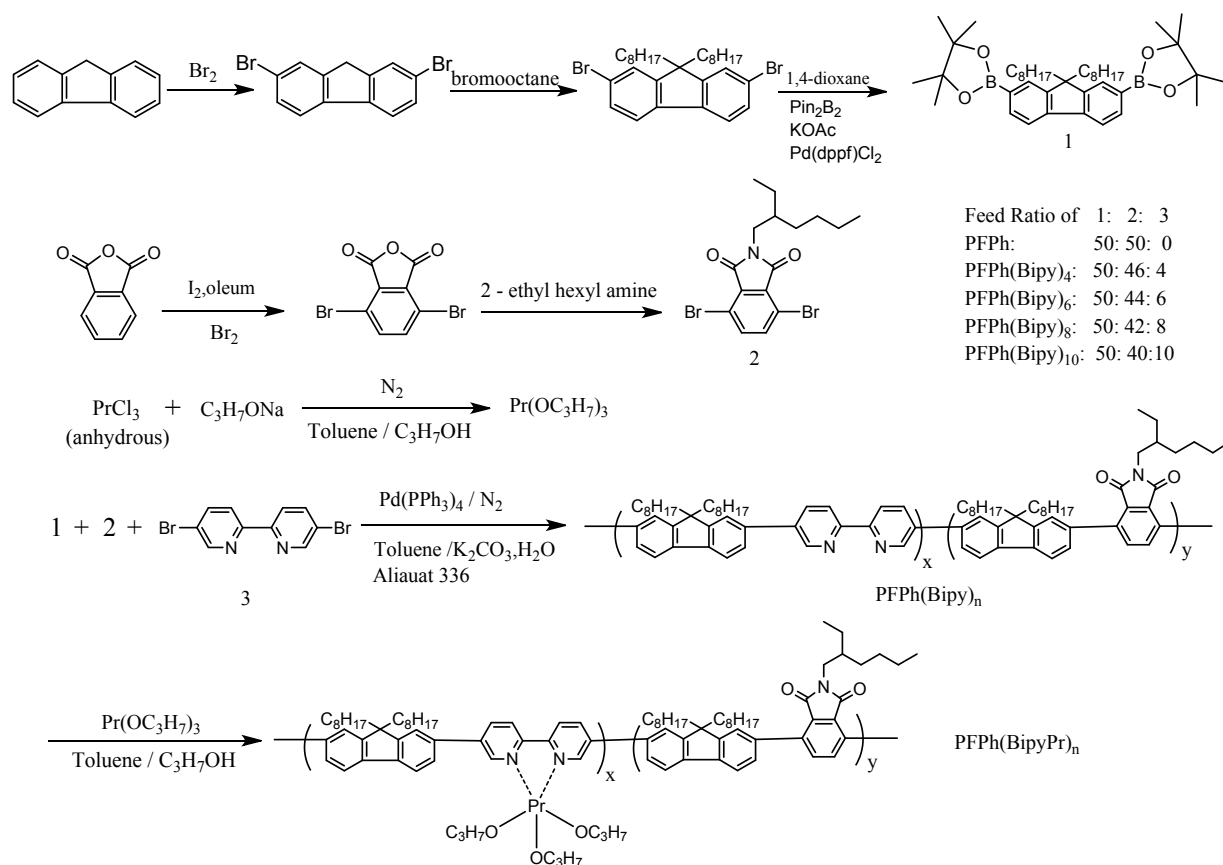
Wei Lv, Huijiao Liu, Wen Wang*, E Yang, Hongyu Zhen and Qidan Ling*

*College of Chemistry and Chemical Engineering, College of Materials Science and Engineering, Fujian Key Laboratory of
Polymer Materials, Fujian Normal University, Fuzhou 350007, China*

1. Synthesis of the monomers and polymers

The monomer 9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) was synthesized according to literature method.¹ Phthalimide (Ph) monomer was prepared in two steps according to literature method.²

The synthetic routes are shown in Scheme 1. A general procedure of polymerization was used for the synthesis of the Pr-free polymers (PFPh, PFPh(Bipy)_n). Under the protection of nitrogen, 9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester), N-(2-ethyl hexyl)-3,6-dibromom-phthalimide, 5,5'-disbromo-2,2'-bipyridine, 5.0 mol% [Pd(PPh₃)₄] and toluene, 2 mol·L⁻¹ aqueous solution of K₂CO₃ and Aliquat 336 as phase transfer catalyst were added to a round-bottom flask. The mixture was vigorously stirred at 110°C for 72 h. Bromobenzene was dropped to react for 6 h and phenylboronic acid was dropped to end-cap the polymer for 6 h. After the mixture was cooled to room temperature, it was slowly added dropwise to methanol. A fibrous solid was obtained by filtration. The solid was washed in a Soxhlet extractor with methanol and acetone for 3 d to remove oligomers and catalyst residues. The resulting polymers were collected and dried under vacuum.



Scheme 1 Synthetic routes and molecular structures of the polymers (PFPh, PFPh(Bipy)_n, PFPh(BipyPr)_n).

PFPh

9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.1951 g, 0.300 mmol), N-(2-ethyl hexyl)-3,6-dibromom-phthalimide (0.1260 g, 0.300 mmol) were used in polymerization (0.1413 g, 72.4% yield).

$^1\text{H NMR}$ (400MHz, CDCl_3) δ (ppm): 7.89-6.93 (m, ArH), 3.55 (s, CH_2), 2.08-0.81 (br, CH_2 , CH_3)

PFPh(Bipy)₄

9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.1928 g, 0.300 mmol), N-(2-ethyl hexyl)-3,6-dibromom-phthalimide (0.1150 g, 0.276 mmol), 5,5'-disbromo-2,2'-bipyridine (0.0076 g, 0.024 mmol) were used in polymerization (0.0847 g, 44.2% yield).

$^1\text{H NMR}$ (400MHz, CDCl_3) δ (ppm): 9.08 (s, ArH), 8.60 (s, ArH), 8.17 (s, ArH), 7.90-6.93 (m, ArH), 3.55 (s, CH_2), 2.08-0.81 (br, CH_2 , CH_3)

PFPh(Bipy)₆

9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.3224 g, 0.500 mmol), N-(2-ethyl hexyl)-3,6-dibromom-phthalimide (0.1839 g, 0.440 mmol), 5,5'-disbromo-2,2'-bipyridine (0.0193 g, 0.06 mmol) were used in polymerization (0.1483 g, 46.8% yield).

$^1\text{H NMR}$ (400MHz, CDCl_3) δ (ppm): 9.09 (s, ArH), 8.61 (s, ArH), 8.18 (s, ArH), 7.89-6.95 (m, ArH), 3.56 (s, CH_2), 2.10-0.84 (br, CH_2 , CH_3)

PFPh(Bipy)₈

9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.3218 g, 0.500 mmol), N-(2-ethyl hexyl)-3,6-dibromom-phthalimide (0.1752 g, 0.420 mmol), 5,5'-disbromo-2,2'-bipyridine (0.0252 g, 0.080 mmol) were used in polymerization (0.1660 g, 52.8% yield).

$^1\text{H NMR}$ (400MHz, CDCl_3) δ (ppm): 9.08 (s, ArH), 8.59 (s, ArH), 8.16 (s, ArH), 7.89-6.92 (m, ArH), 3.54 (s, CH_2), 2.08-0.80 (br, CH_2 , CH_3)

PFPh(Bipy)₁₀

9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.3221 g, 0.500 mmol), N-(2-ethyl hexyl)-3,6-dibromom-phthalimide (0.1669 g, 0.400 mmol), 5,5'-disbromo-2,2'-bipyridine (0.0316 g, 0.100 mmol) were used in polymerization (0.1623 g, 52.1% yield).

$^1\text{H NMR}$ (400MHz, CDCl_3) δ (ppm): 9.07 (s, ArH), 8.61 (s, ArH), 8.15 (s, ArH), 7.89-6.92 (m, ArH), 3.54 (s, CH_2), 2.07-0.80 (br, CH_2 , CH_3)

The following procedure was adopted for the synthesis of Pr-coordinated polymers (PFPh(BipyPr)_n).

Pr triisopropoxide was synthesized from anhydrous Pr chloride (Scheme 1). The isopropoxy groups of the salt can be easily substituted by chelators to form a Pr complex in anhydrous organic solvents.

Under a nitrogen atmosphere, polymer (0.0500 g), Pr triisopropoxide and toluene were mixed together in a round-bottom flask. After the solid was dissolved, the solution was refluxed for 1 d. The reactant was cooled down to room temperature and was poured into methanol and filtered. The crude product was extracted by Soxhlet extractor with chloroform. The fraction from chloroform was concentrated under reduced pressure and precipitated into methanol. The resulting polymer was collected and dried under vacuum.

PFPh(BipyPr)₄

0.0432 g, 86.3% yield; ¹H NMR (400MHz, CDCl₃) δ (ppm): 9.22 (s, ArH), 8.10 (s, ArH), 7.89-6.92 (m, ArH), 3.55 (s, CH₂), 2.07-0.80 (br, CH₂, CH₃)

PFPh(BipyPr)₆

0.0450 g, 88.0% yield; ¹H NMR (400MHz, CDCl₃) δ (ppm): 7.87-7.62 (m, ArH), 3.54 (s, CH₂), 2.04-0.82 (br, CH₂, CH₃)

PFPh(BipyPr)₈

0.0430 g, 86.8% yield; ¹H NMR (400MHz, CDCl₃) δ (ppm): 9.07 (s, ArH), 8.58 (s, ArH), 8.16 (s, ArH), 7.89-6.92 (m, ArH), 3.54 (s, CH₂), 2.08-0.80 (br, CH₂, CH₃)

PFPh(BipyPr)₁₀

0.0440 g, 85.0% yield; ¹H NMR (400MHz, CDCl₃) δ (ppm): 9.07 (s, ArH), 8.58 (s, ArH), 8.16 (s, ArH), 7.89-6.92 (m, ArH), 3.54 (s, CH₂), 2.08-0.80 (br, CH₂, CH₃)

Figure S1 shows the ¹H NMR spectra of PFPh, PFPh(Bipy)_n. Figure S2 shows the ¹H NMR spectra of PFPh(BipyPr)_n.

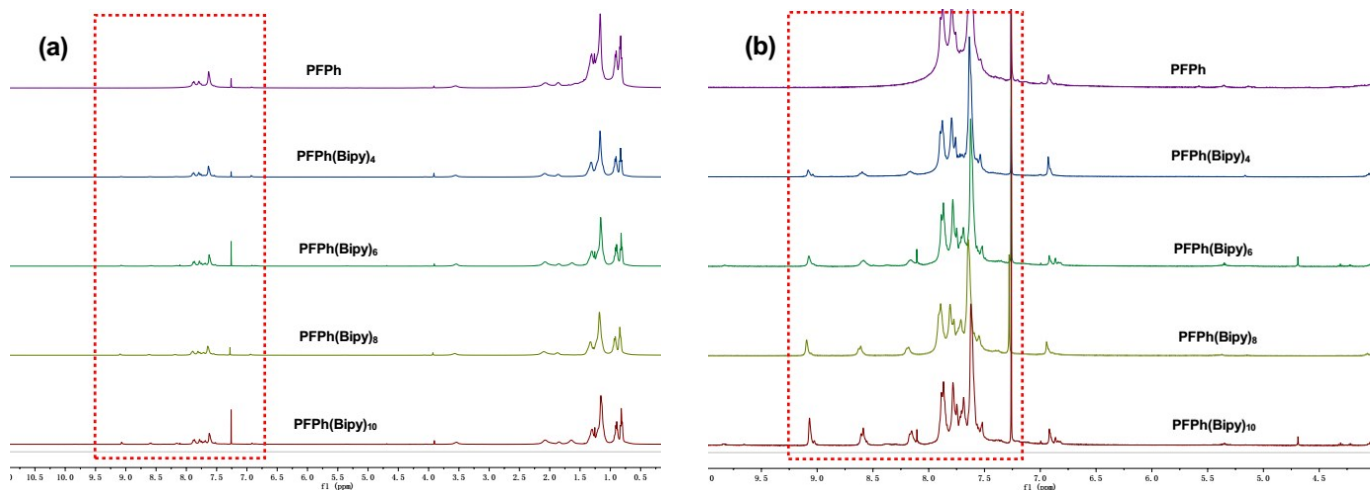


Figure S1 ^1H NMR spectra of the polymers (PFPh, PFPh(Bipy) $_n$): (a) full figure; (b) detail view.

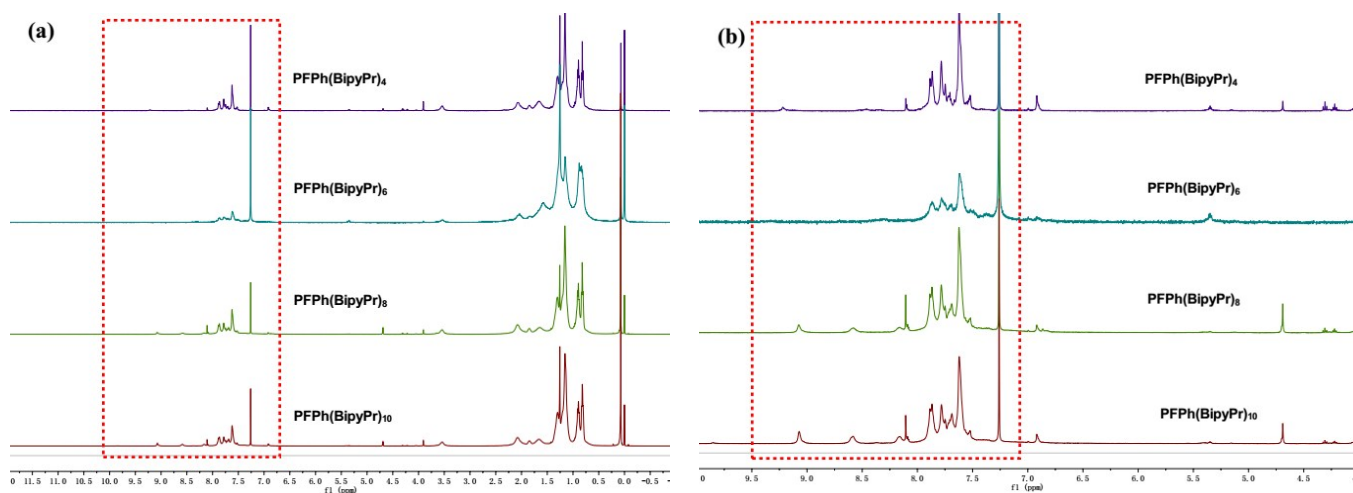


Figure S2 ^1H NMR spectra of the polymers (PFPh(BipyPr) $_n$): (a) full figure; (b) detail view.

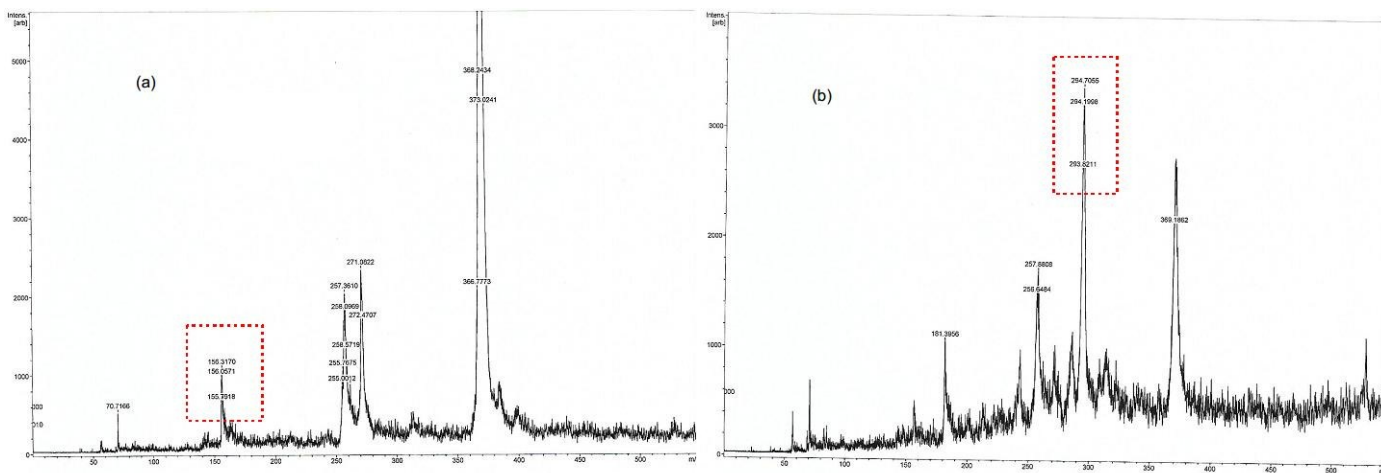


Figure S3 Mass spectra of the polymers PFPh(Bipy) $_{10}$ (a) and PFPh(BipyPr) $_{10}$ (b).

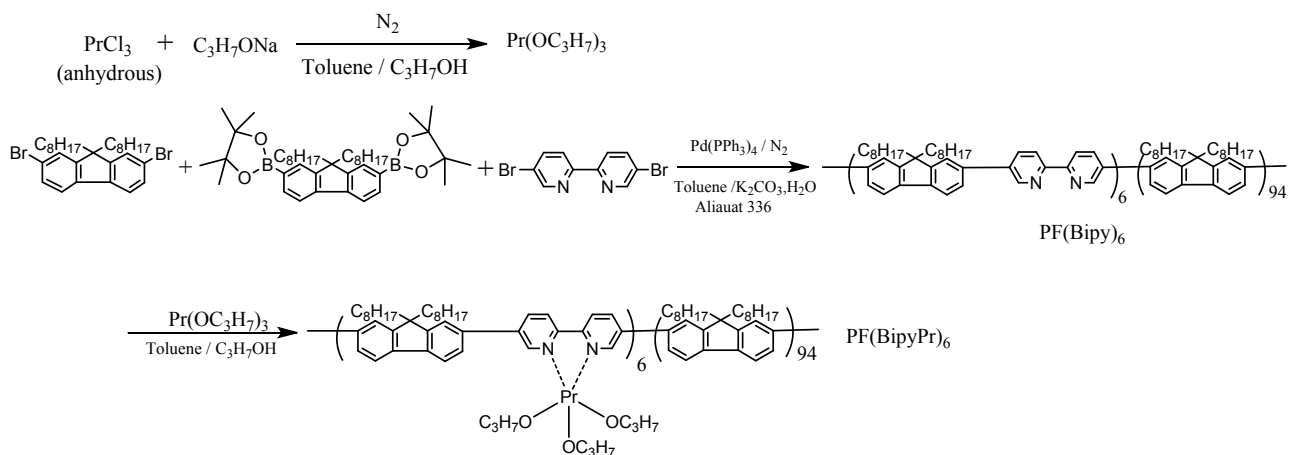
For comparison, the polymer PF(BipyPr) $_6$ without Ph moiety was also synthesized by similar reactions. The synthetic route is shown in Scheme 2. First, PF(Bipy) $_6$ was synthesized with 2,7-disubromo-9,9'-dioctylfluorene, 9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) and 5,5'-disubromo-2,2'-bipyridine

by Suzuki coupling reaction. The Pr-coordinated polymer PF(BipyPr)₆ was obtained by coordination reaction with polymer PF(Bipy)₆ and Pr triisopropoxide.

Under the protection of nitrogen, 2,7-disbromo-9,9'-dioctylfluorene (0.2415 g, 0.4403 mmol), 9,9'-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.3222 g, 0.5014 mmol), 5,5'-disbromo-2,2'-bipyridine (0.0192 g, 0.0612 mmol), 5.0 mol% [Pd(PPh₃)₄] and toluene, 2 mol·L⁻¹ aqueous solution of K₂CO₃ and Aliquat 336 as phase transfer catalyst were added to a round-bottom flask. The mixture was vigorously stirred at 110°C for 72 h. Bromobenzene was dropped to react for 6 h and phenylboronic acid was dropped to end-cap the polymer for 6 h. After the mixture was cooled to room temperature, it was slowly added dropwise to methanol. A fibrous solid was obtained by filtration. The solid was washed in a Soxhlet extractor with methanol and acetone for 3 d to remove oligomers and catalyst residues. The resulting polymers PF(Bipy)₆ were collected and dried under vacuum (0.2834 g, 75.7% yield).

Under a nitrogen atmosphere, PF(Bipy)₆ (0.0500 g), Pr triisopropoxide and toluene were mixed together in a round-bottom flask. After the solid was dissolved, the solution was refluxed for 1 d. The reactant was cooled down to room temperature and was poured into methanol and filtered. The crude product was extracted by Soxhlet extractor with chloroform. The fraction from chloroform was concentrated under reduced pressure and precipitated into methanol. The resulting polymer PF(BipyPr)₆ was collected and dried under vacuum (0.0472 g, 90.1% yield).

¹H NMR (400 MHz, CDCl₃), δ(ppm): 9.12 (br, ArH), 8.57–8.11 (br, ArH), 7.86–7.36 (m, ArH), 2.12 (br, CH₂), 1.64 (br, CH₂), 1.26–1.14 (br, CH₂), 1.00–0.80 (br, CH₃). *M_n*: 2.2 × 10⁴, *M_w*: 4.8 × 10⁴, PDI: 2.13.



Scheme 2 Synthetic route and molecular structure of the polymer (PF(BipyPr)₆).

2. Optical properties

The UV-vis absorption spectra recorded from thin films are shown in Figure S4. The UV-vis spectra of PFPh(Bipy)_n, PFPh(BipyPr)_n in thin-film were similar and dominated by a single absorption peak at around 363-370 nm, which could be attributed to the π - π^* transition from the conjugated polymer backbone. As Pr was coordinated to the polymer, the absorption peak slightly broadened and the absorption tails extended to a longer wavelength, suggesting the stronger inter-chain interaction due to the Pr atom on the backbone.

The optical band gaps of the polymers estimated from the film absorption onset are around 2.48-2.68 eV. With the increase of Bipy and Pr content in the polymers, the optical band gap of the polymers decreased gradually.

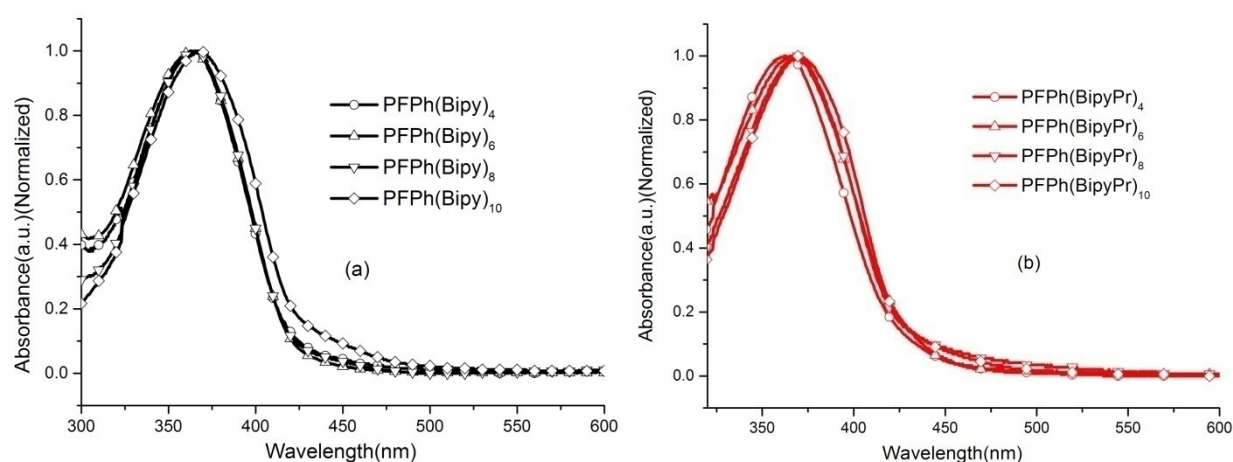


Figure S4 UV-vis absorption spectra of polymers (in film) (a) PFPh(Bipy)_n; (b) PFPh(BipyPr)_n.

The optical and electrochemical data of the polymers are shown in Table S1.

Table S1 Optical and Electrochemical properties of polymers

Polymer	$\lambda_{\text{abs}}(\text{nm})$ (film)	$\lambda_{\text{em}}(\text{nm})$ (film)	$E_{\text{g}}^{\text{opt}}$ (eV)	$E_{\text{ox}}^{\text{onset}}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
PFPh(Bipy) ₄	363	468	2.68	+1.14	-5.56	-2.88

PFPh(Bipy)₆	363	470	2.65	+1.19	-5.61	-2.98
PFPh(Bipy)₈	366	488	2.58	+1.34	-5.76	-3.18
PFPh(Bipy)₁₀	368	469	2.54	+1.40	-5.82	-3.28
PFPh(BipyPr)₄	363	476	2.64	+1.10	-5.52	-2.88
PFPh(BipyPr)₆	366	477	2.58	+1.15	-5.57	-2.99
PFPh(BipyPr)₈	367	494	2.52	+1.39	-5.81	-3.29
PFPh(BipyPr)₁₀	370	493	2.48	+1.44	-5.86	-3.38

^a Optical band gaps were calculated from the onset of film absorption.

(λ_{abs} : the maximum absorption wavelength; λ_{em} : the maximum emission wavelength)

References

- [1] L. Wang, W. Wang, W. Zhang, E. Kang and W. Huang, *Chem. Mater.*, 2000, **12**, 2212.
 [2] X. Guo, F. S. Kim, S. A. Jenekhe and M. D. Watson, *J. Am. Chem. Soc.*, 2009, **131**, 7206.