Poly[2,7-(9-oxo-9-phosphafluorenylene)-*alt-co*-(1,4-arylene)]s: Phosphorus-containing π-Conjugated Polymers

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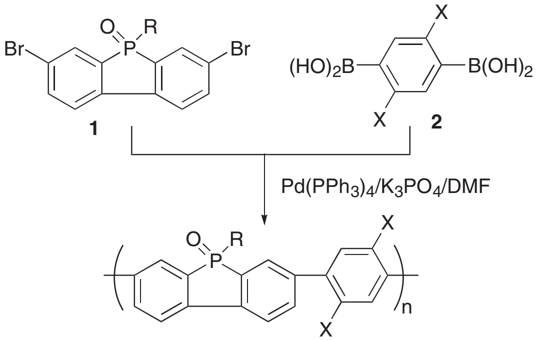
Poly[2,7-(9-oxo-9-phosphafluorenylene)-*alt-co*-(1,4-arylene)]s, readily prepared from 2,7-dibromo-9-oxo-9-phosphafluorenes and arylene bisboronates, behaved as extended π-conjugated polymers in the UV–vis absorption spectroscopy and displayed green-blue fluorescence with high quantum yields. Cyclic voltammetry revealed the polymers exhibited electrochromic behaviors and afforded a bandgap of ca. 2.8 eV, consistent with the value from the absorption edge.

Phosphorus-containing polymers for heterogenized homogeneous catalysts have been extensively studied. However, the research aiming at their use in electronic applications is still very limited.[1] Theoretical study on cyclopentadiene and phosphole-(1-phosphacyclopentadiene) has revealed that the latter displays a red-shift in UV–vis spectroscopy as compared with the former.[2] On the other hand, 9-oxo-9-phosphafluorene, having a oxo-phosphole core, possesses high planarity,[3] a prerequisite for extended π-conjugation. In addition, the electronic behavior of oxo-phospholes is envisioned to be affected by coordination of metal species. Accordingly oxophospholes are an interesting class of compounds in electronic applications. However, oxophosphole-containing polymers have never been documented while only limited number of phosphole-containing polymers[1a,d] and short oligomers[4] have been synthesized. During our study on the properties of 9-oxo-9-phosphafluorene-containing polymers[5] to explore superiority over the parent fluorene-containing polymers,[6] Wu, Réau, and co-workers very recently disclosed light-emitting behaviors of monomeric phospholes and their sulfide analogs.[7] This paper promted us to report our own results in this area of research.

Palladium-catalyzed coupling polymerization of 2,7-dibromo-9-oxo-9-phosphafluorenes (**1**) with arylene bisboronates (**2**) readily afforded poly[2,7-(9-oxo-9-phosphafluorenylene)-*alt-co*-(1,4-arylene)]s (**3**) as light-green solids; yields and molecular weight data are listed in Table 1.[8] The polymerization worked well in DMF in the presence of K_3PO_4, but did not proceed at all in the two-phase media such as toluene/aq K_2CO_3, resulting in a quantitative recovery of the starting bromide. Polymers **3a** and **3c** are soluble in $CHCl_3$, chlorobenzene, and THF, but not in acetonitrile and toluene, while **3b** and **3d** are less soluble in $CHCl_3$ and chlorobenzene and only partially soluble in THF. Accordingly GPC analyses of the THF-soluble fractions of **3b** and **3d** showed lower *n* values (11 and 6, respectively) as compared with the values estimated on the basis of their elemental analysis data (14 and 9, respectively). ^{31}P NMR spectroscopy of **3a** displayed a single peak at 43.9 ppm, close to the



3a: R = $^nC_9H_{19}$, X = $^nC_6H_{13}O$
3b: R = $^nC_3H_7$, X = $^nC_6H_{13}O$
3c: R = $^nC_6H_{13}(CH_3)CH$, X = $^nC_6H_{13}O$
3d: R = $^nC_9H_{19}$, X = H

Table 1. Yield and molecular weight of polymers **3**

Polymer	Yield/%	M_n[a]	M_w[a]	M_w/M_n	n[b]
3a	83	10100	22000	2.18	17 (13)
3b	89	6230	8980	1.44	11 (14)
3c	90	19400	31100	1.60	32 (22)
3d	80	2110	2380	1.13	6 (9)

[a]Determined by GPC using polystyrene standards and THF eluent. [b]Average number of the repeat units in the polymer, calculated from M_n obtained from GPC. The figures in parentheses are the values estimated from the elemental analysis.

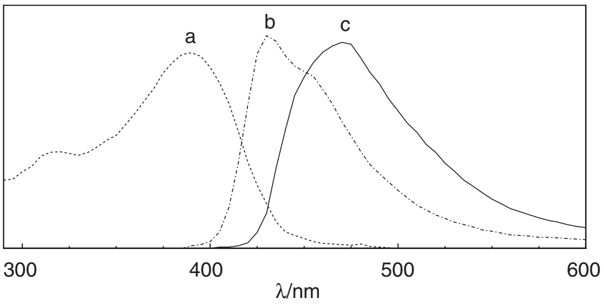


Figure 1. UV–vis absorption (a, film) and fluorescence (b, $CHCl_3$ solution; c, film) spectra of polymer **3a**.

Table 2. Optical properties of the polymers **3**

	$CHCl_3$ solution[a]				film[b]		
3	λ_{abs}/nm	$\log \varepsilon$	λ_{fl}/nm	Φ_{fl}	λ_{abs}/nm	λ_{fl}/nm	E_g/eV
3a	384	4.41	431	0.756	390	472	2.75
3b	386	4.47	433	0.719	395	465	2.78
3c	386	4.47	432	0.681	387	465	2.78
3d	386	4.50	413	0.809	386	457	2.88

[a]The concentration was 1.0×10^{-5} mol dm^{-3} per repeat unit. [b]On a quartz plate.

chemical shift of authentic 9-nonyl-9-oxo-9-phosphafluorene (+44.4 ppm). Elemental analyses suggested that both termini of polymers **3** are brominated 9-oxo-9-phosphafluorene rings.

As illustrated in Figure 1, the UV–vis absorption spectrum of **3a** in solid state (thin film on quartz substrate prepared by spin-coating from a 1% 1,2-dichloroethane solution) shows a $\lambda_{\max(\mathrm{abs})}$ at 390 nm with an onset of absorption at ca. 460 nm. The absorption peak in dilute chloroform is slightly blue-shifted to 384 nm (Table 2). These absorption peaks in solid state and solution are very much red-shifted relative to 9-nonyl-9-oxo-9-phosphafluorene, which exhibits $\lambda_{\max(\mathrm{abs})}$ at 325 and 327 nm in $CHCl_3$ and solid state, respectively. As summarized in Table 2 the absorption behavior of the other polymers is basically similar to that of **3a**. The π–π^* bandgap of **3** (E_g) calculated from the absorption edge in solid state ranges from 2.75 to 2.88 eV, which is smaller than those of the fluorenylene-*alt-co*-phenylene copolymers (3.00 eV).[6e]

PL spectra of polymers **3** in chloroform display a $\lambda_{\max(\mathrm{fl})}$ in the region of 413–433 nm with vibronic sidebands in quite high quantum yields (Φ_{fl}) ranging from 0.681 to 0.809.[9] The small Stokes shift in solution is presumably associated with the rigidity of the polymer structure, which allows efficient emission without changing the molecular geometry. In solid state the emission is 32–44 nm red-shifted ($\lambda_{\max(\mathrm{fl})} = 457$–$472$ nm) as compared with the values in solution, suggesting a more delocalized excited state in the solid phase.[6f] The $\lambda_{\max(\mathrm{fl})}$ values are much higher than those of fluorenylene-*alt-co*-phenylene polymers.[6e,f] It is noteworthy, however, that no interchain excimer emission is observed even in solid state[10] whereas fluorenylene-*alt-co*-phenylene and related polymers show excimer emission in the region of 513–534 nm.[6e–g] The high quantum yield of the blue emission (vide supra) as compared with the fluorenylene-*alt-co*-phenylene polymers may be associated with the lack of the excimer emission.

Cyclic voltammetry of **3** has revealed that they display electroactivity upon reduction and oxidation of a film cast on a glassy carbon disc working electrode (ca. 0.28 cm^2) in a 0.10 $\mathrm{mol\,dm^{-1}}$ tetrabutylammonium perchlorate solution of acetonitrile at room temperature (Figure 2). Polymer **3a** showed an onset of reduction at ca. −2.06 V vs Ag/Ag^+ (electrochemical potential 0.25 V vs SCE), and reduction/reoxidation waves ($E_{\mathrm{pc}} = -2.46/E_{\mathrm{pa}} = -2.35$ and -2.23 V). The reduction/reoxidation process was reversible. Interestingly **3a** exhibits electrochromic behaviors; the color of **3a** (film coated on a platinum plate) changed from light green to deep violet upon reduction. Spectroelectrochemical measurement of a film of **3a** on an ITO plate has revealed that, upon reduction beyond −2.20 V, a new absorption band emerges at 545 nm[11] while the intensity of the 390 nm band decreases. On the other hand, **3a** shows an onset of oxidation at ca. 0.75 V and the anodic peak is observed at 1.06 V. However, the oxidative reaction is irreversible and the film turns brown. The HOMO and LUMO levels[12] of **3a** on the basis of the oxidation and reduction onsets are estimated at 5.4 and 2.6 eV, respectively, resulting in a bandgap of 2.8 eV, which is in good agreement with the value from the absorption edge (2.75 eV). The HOMO level is slightly higher than that of the fluorene analogue (5.66 eV) while the LUMO is almost the same (2.62 eV).[6e]

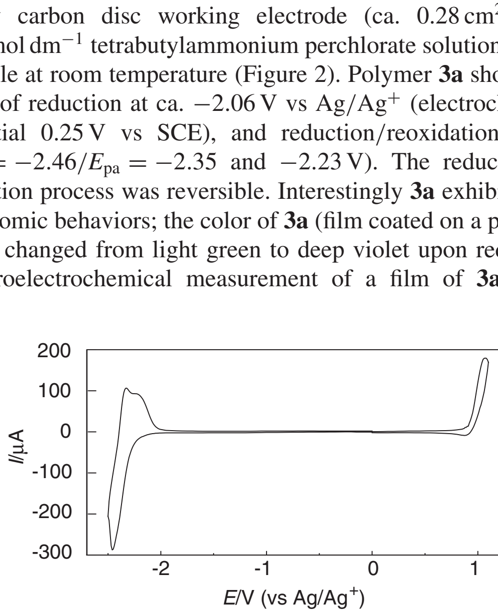


Figure 2. Cyclic voltammogram of polymer **3a** (scanning rate = 50 $\mathrm{mV\,s^{-1}}$) in the solution of tetrabutylammonium perchlorate (0.10 $\mathrm{mol\,dm^{-1}}$) in MeCN at room temperature.

Application to OLED is now in progress.

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8 General procedure for the synthesis of poly[2,7-(9-oxo-9-phosphafluorenylene)-*alt-co*-(1,4-arylene)]s: Under N_2 atmosphere, a mixture of 2,7-dibromo-9-oxo-9-phosphafluorene **1** (1.0 mmol), 1,4-arylene bisboronate **2** (1.0 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), K_3PO_4 (2.0 g), and *N*,*N*-dimethylformamide (10 mL) in a Schlenk tube was stirred for 48 h at 125 °C. The resulting mixture was poured into H_2O (100 mL), and the mixture was filtered to obtain light green solids. The solids were dissolved in $CHCl_3$ (100 mL), filtered and the filtrate was concentrated to approximately 5 mL under vacuum and poured into methanol (100 mL) to precipitate solids of polymer **3**, which were collected by filtration and dried under vacuum for several days.

9 Monomeric phosphafluorenes do not display emission. The Φ_{fl} values of polymers **3** were determined by using (−)-quinine standard ($\Phi_{\mathrm{fl}} = 0.546$). See D. F. Eaton, *Pure Appl. Chem.*, **60**, 1055 (1988).

10 The lack of excimer emission may be associated with the presence of the rather long alkyl chain bound to phosphorus.

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