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Synthesis, Optical Properties, and Characterization of New Soluble Conjugated Poly(*p*-phenylenevinylene) Derivatives Constituted of Alternating Pyrazole and 1,3,4-Oxadiazole Moieties

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Two new soluble poly(*p*-phenylenevinylene) derivatives with 1,3,4-oxadiazole and pyrazole rings along the main core were successfully synthesized by 1,3-dipolar addition, dehydration, and Heck coupling reaction. The new conjugated polymers are soluble in common organic solvents afforded by the fully conjugated backbone with soluble dedecyloxy side groups. The polymers showed relatively high glass-transition temperatures (~150°C) and good satisfactory thermal stability. Solutions of the polymers emitted bluish-green light with photoluminescence (PL) emission maxima around 530–540 nm. The PL spectrum for polymers of thin films, with a maximum at 570 nm, shows a red-shift (~35 nm) with respect to the solution spectrum. Cyclic voltammetry displayed that both conjugated polymers had reversible reduction and irreversible oxidation, making them n-type electroluminescent materials. The electron affinity of new polymers was estimated as 2.76–2.81 eV. The weight-average molecular weights (M_w) of the new soluble polymers were in the range 3400–3500.

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Introduction

Since the first poly(*p*-phenylenevinylene) (PPV) was developed as a polymer light-emitting diode (PLED),[1–12] the π-conjugated polymeric derivatives have been studied extensively because of their multifunctional application.[11–17] Typically, conjugated polymers such as PPV, poly(thiophene) (PT), and their derivatives tend to p-type, that is, they favour hole-transport.[18,19] Because of the scarcity of known polymers with good soluble activity and electron-injection capability, soluble π-conjugated electroluminescent polymers that contain electron-withdrawing units in the main chain or at side groups have been targeted in the development of polymers with improved electron-transport capability.

Aromatic 1,3,4-oxadiazole-based conjugated polymers have been shown to be promising candidates for light-emitting devices because of their thermal, hydrolytic, and photo stability,[20–25] electron affinity, and hole-blocking ability.[19,26,27] 1,3,4-Oxadiazole-based heterocyclic conjugated polymers were also enthusiastically investigated to improve the electron injection, transport properties, and to confer rigidity, for example, 1,3,4-oxadiazole–carbazole[28] and 1,3,4-oxadiazole–pyridine.[29]

In our previous work, the chromophore of pyrazole played an assistant role in controlling the fundamental electroluminescent process and 1,3,4-oxadiazole-based pyrazole derivatives were revealed as efficient blue-greenish electroluminescent materials.[30] As a result, we introduced pyrazole units into the main chain of 1,3,4-oxadiazole-based conjugated polymers as the chromophore to improve the electron-transporting properties, as pyrazole is an electron-rich heterocycle.[30] Sydnones are an important and frequent structural feature in organic chemistry. In this work, sydnones underwent 1,3-dipolar addition[30] with acetylenedicaboxylate to provide functional pyrazole compounds. These new soluble PPV-based conjugated polymers with 1,3,4-oxadiazole and pyrazole rings in the backbone were successfully synthesized by dehydration[31] and Heck coupling[29] from the functional pyrazole intermediates.

Result and Discussion

Synthesis

The synthetic route is shown in Scheme 1 for the generation of two 1,3,4-oxadiazole-based pyrazole monomer derivatives **5a** and **5b**. Considering the large-scale preparation of sydnone substrates, the commercial available raw materials hydrazine with various *para*-H, and -OMe substituent groups were selected as the starting materials to synthesize sydnone compounds **1a** and **1b**. Sydnone **1a** and **1b** were prepared by following the procedure developed by our laboratory.[32] Sydnone compounds **1a** and **1b** with various substituents on the *N*1-phenyl

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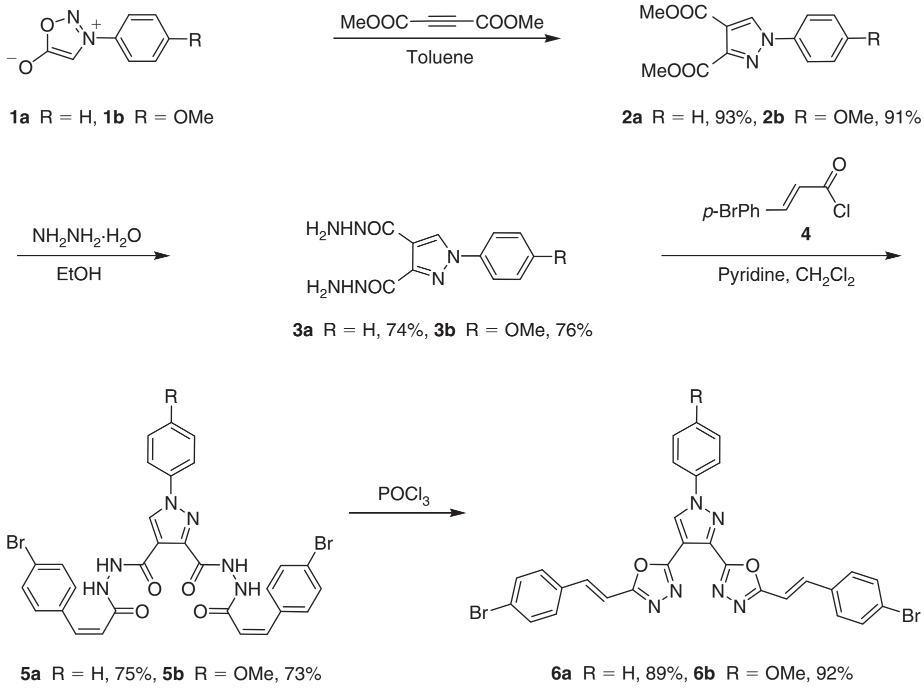
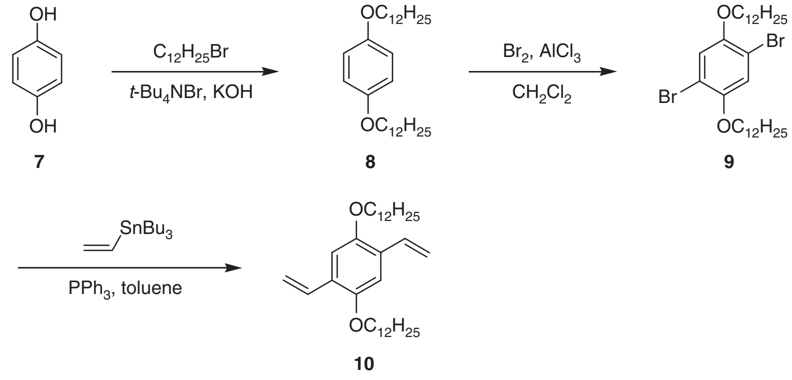


Scheme 1.



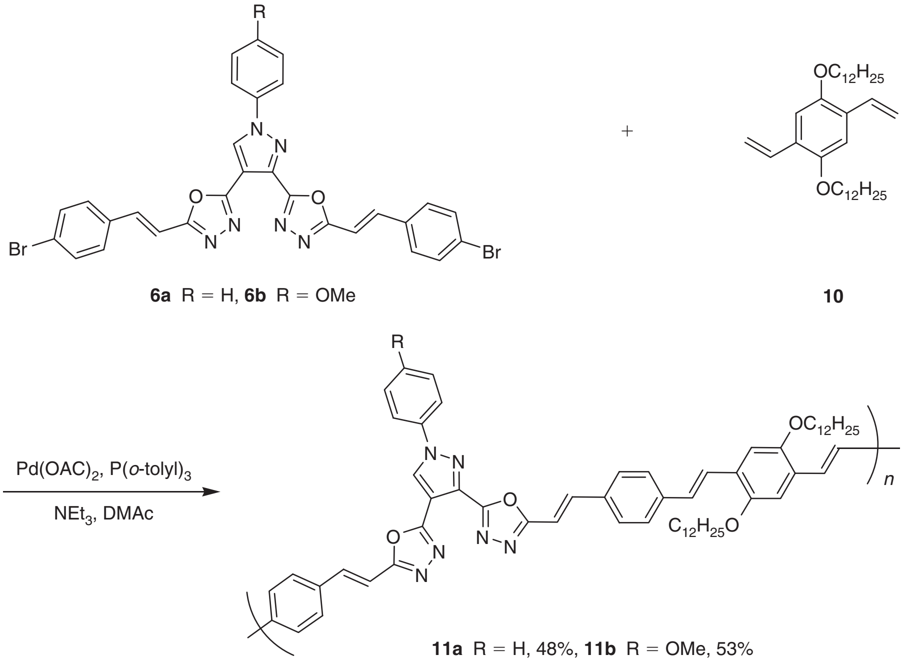
Scheme 2.

group, including *para*-H, and -OMe groups were applied to dimethyl acetylenedicaboxylate (DMAD) to give the corresponding dimethyl 1-aryl-1*H*-pyrazole-3,4-dicarboxylate **2a** and **2b** as a white solid in almost quantitative yields (91–93%).[33] This 1,3-dipolar cyclization has proved to be an efficient and economical way to provide the pyrazole derivatives. Treating 1-aryl-1*H*-pyrazole-3,4-dicarboxylate **2a** and **2b** with hydrazine hydrate at reflux afforded the corresponding dihydrazide product **3a** and **3b** in good yield (74–76%) according to published reports.[34]

3-(4-Bromophenyl)acrylic acid was efficiently transformed into the corresponding 3-(4-bromophenyl)acryloyl chloride **5** in 72% yield by using pyridine and thionyl chloride in CH_2Cl_2 at 0°C to room temperature for 3 h. Dihydrazide compounds **3a** and **3b** were treated with 3-(4-bromophenyl)acryloyl chloride **4** in CH_2Cl_2 at room temperature for 2–3 h to give the corresponding bis(trihydrazide) products **5a** and **5b** in 73–75% yields.[35] Compounds **5a** and **5b** underwent dehydration–cyclization to form the 1,3,4-oxadiazole-based pyrazole derivatives **6a** and **6b** in 89–92% excellent yields[31] in the presence of $POCl_3$.

The synthetic route of 1,4-didodecyloxy-2,5-divinylbezene **10** is outlined in Scheme 2. 1,4-Dibromo-2,5-didodecyloxybezene **9** was easily synthesized in two steps with a total yield of 64% using 1,4-hydroxybezene **7** as starting material following the reported procedure.[36] Eventually, Stille coupling of 1,4-dibromo-2,5-didodecyloxybezene **9** with 2.2 equiv. of vinyltin reagent was performed to give the coupled product 1,4-didodecyloxy-2,5-divinylbezene **10** in good yield (73%).[37]

Soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **11b** were synthesized by the Pd-catalyzed Heck coupling reaction of 1,3,4-oxadiazole-based pyrazole derivatives **6a** and **6b** with divinyl compound **10** in 63–71% crude yields (Scheme 3).[38] After hot filtration and further recrystallization, the pure yellow wool-like solid products **11a** and **11b** were provided in 48–53% yields. The two polymers were soluble in common organic solvents such as chloroform, dichloromethane, dimethylformamide (DMF), toluene, tetrahydrofuran (THF), and xylene, etc. Structural characterization of the polymers was accomplished by gel permeation chromatography (GPC), FT-IR, ^{13}C and ^{1}H NMR spectroscopy, and elemental analysis.



Scheme 3.

Table 1. Characterization of the soluble 1,3,4-oxadiazole-based conjugated polymers 11a and 11b

Conjugated polymer	GPC M_w	Absorbance λ_{max} [nm]			Emission λ_{max} (PL) [nm]		
		CH_2Cl_2	Toluene	Film	CH_2Cl_2	Toluene	Film
11a	3589	340, 416	338, 410	344, 417	541	532	569
11b	3421	335, 404	330, 397	336, 416	541	529	573

The weight-average molecular weights (M_w) of the new synthetic polymers, as determined by GPC using polystyrene standards, were in the range of 3400–3500 (Table 1). The presence of the dodecyloxy side chain[39] and the Heck coupling polymerization,[40] gave rise to the relatively low molecular weights of the copolymer. The results are consistent with the reported literature data.[40,41]

Optical Properties

The new soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **11b** exhibited very similar absorption spectra as shown in Table 1 and Figs 1 and 2. They all show two main strong absorption peaks: one in the visible range at ~415 nm and the other in the UV region at ~340 nm. Compared with that of PPV that contained 1,3,4-oxadiazole (OX1-PPV, the λ_{max} values are 328 and 393 nm in THF solution or in a thin film),[29] the UV absorption peak of the new polymers **11a** and **11b** is blue-shifted by 12 nm, whereas the visible absorption peak is red-shifted by 22 nm as a result of the introduction of the pyrazole chromophore. The absorption at 340 nm can be assigned to the π–π* transition of the cross-conjugated oxadiazole segment, which are the same absorption maximums of the monomers **6a** and **6b**.[30] The identical absorption maximums of the oxadiazole units before and after the polymerization imply that, in dilute solutions, the electronic interactions between the oxadiazole units and the PPV backbone are rather limited.[38] Apparently, the oxadiazole rings are twisted away from the plane of the conjugated backbone. The absorption at 403 nm was initially assigned to the π–π* transition of the conjugated polymer backbone.

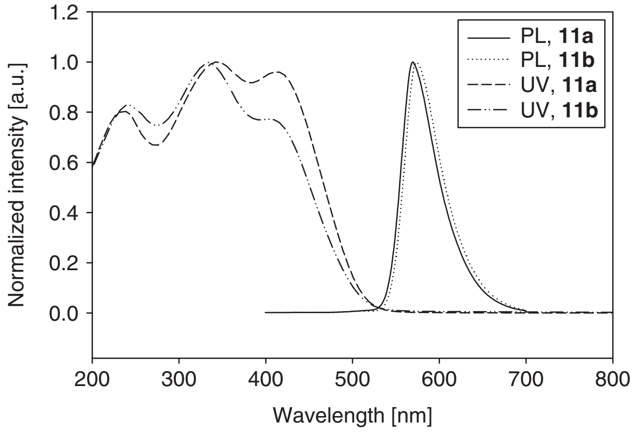


Fig. 1. The UV-vis and PL spectra of **11a** and **11b** in CH_2Cl_2 solution.

Figures 1 and 2 show the photoluminescence (PL) spectra of the new soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **11b**. The polymer exhibited a maximum emission at ~540 nm in organic solvent and at ~570 nm in the thin film, and this emission maximum is clearly independent of the excitation wavelengths. Emissions of the 1,3,4-oxadiazole–pyrazole hybrids[30] at 365–375 nm and the 1,3,4-oxadiazole unit

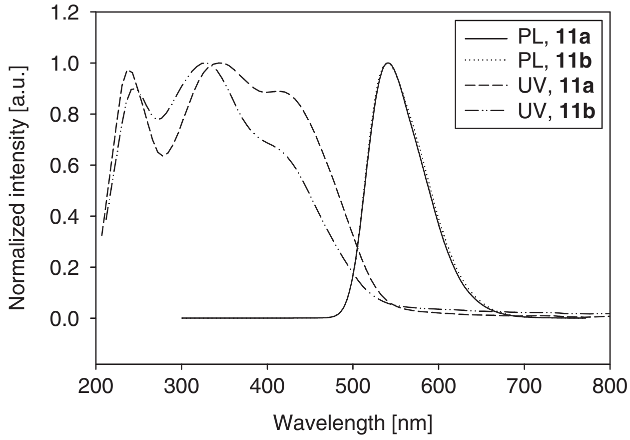


Fig. 2. The UV-vis and PL spectra of **11a** and **11b** in thin film.

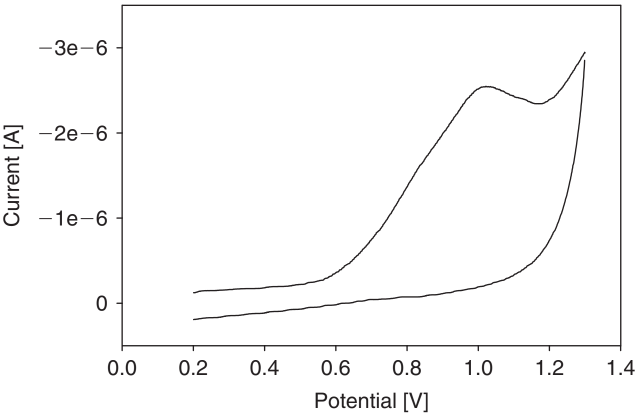


Fig. 3. Cyclic voltammetry of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a**.

at 395 nm were not observed.[29] In summary, the excitation spectra of the new polymers show almost identical maximums to their absorption spectra, which indicates an efficient energy transfer from the oxadiazole moiety to the PPV backbone.

Cyclic Voltammetry Measurements

The electrochemical properties of the new soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **11b** were investigated by cyclic voltammetry, as shown in Figs 3 and 4, and the resulting data are summarized in Table 2. Upon the anodic sweep, **11a** and **11b** show reversible oxidation processes. The bandgap energies of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **1b** are estimated from the onset wavelength (λ_{onset}) of the UV-vis absorption.[12] Compounds **11a** and **11b** have high lowest unoccupied molecular orbital (LUMO) values of ~2.76–2.81 eV and high electron affinities of 2.76–2.81 eV (Table 2).

Thermal Properties

Thermal and thermomechanical characterization of the polymers was investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The glass-transition temperatures (T_gs) of the polymers were determined by the DSC method. No phase transitions were recorded during the first and second heating in the DSC experiments. The absence of a melting endotherm confirmed the amorphous nature of the polymers. The T_g was obtained from the onset temperature of the first inflection point that was recorded during the second heating (Table 3 and Fig. 5). Compounds **11a** and **11b** showed the same T_g (~150°C). We found that the *para*-methoxy withdrawing group on the *N*1-phenyl moiety did not affect the system. The TGA thermograms of the polymers are summarized in Table 3 and Fig. 6. The soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **11b** were stable up to around ~275–300°C in N_2. They afforded a relatively low anaerobic char yield (~35%) at 800°C because of the thermally sensitive alkoxy side groups. Compound **11a** was slightly more thermally stable than **11b**, and all its thermal properties were superior to PPV.

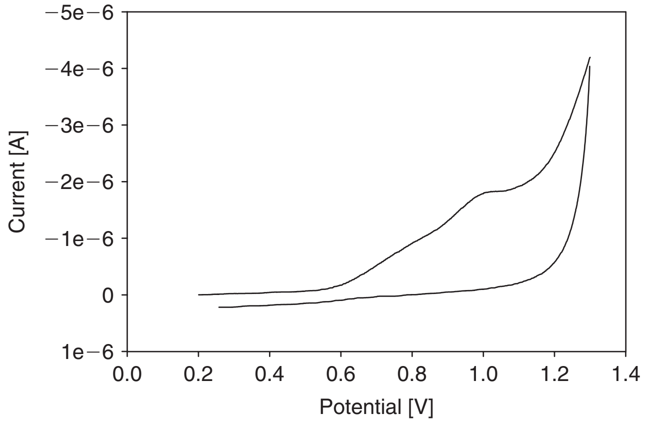


Fig. 4. Cyclic voltammetry of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11b**.

Electroluminescent Properties

A double-layer organic light-emitting diode (OLED) device with a structure of indium tin oxide (ITO)/polythiophene (PEDOT)/**11b**/LiF were constructed by successive vapour deposition of the materials under vacuum onto the ITO-coated glass substrate. The device was tested in air under ordinary laboratory conditions and was found to emit blue-greenish emission at an onset voltage of 9.2 V (Fig. 7). An EL maximum at 544 nm (Fig. 8) was observed for the device and a red shift with a PL maximum at 573 nm in the film.

Conclusions

Two new soluble polymers that contain 1,3,4-oxadiazole and pyrazole rings along the main core were synthesized by a Heck coupling reaction. The polymers were readily soluble in common organic solvents and had a moderate T_g (~150°C) and a good thermal stability. The electron affinity of new polymers was estimated as 2.76–2.81 eV. The new conjugated polymers are soluble in common organic solvents for their fully conjugated backbone with soluble dedecyloxy side groups. The polymers were luminescent with PL emission maxima around 530–540 nm in solution and ~570 nm in a thin film. Cyclic voltammetry displayed that both conjugated polymers had reversible oxidation and irreversible reduction, making them n-type electroluminescent materials. The weight-average molecular weights of the new soluble polymers containing pyrazole and 1,3,4-oxadiazole moieties were in the range of 3400–3500.

Experimental

General Procedure

Sydnones were synthesized according to literature procedures.[32] All chemicals were reagent grade and used

Table 2. Electrochemical properties of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers 11a and 11b

LUMO, lowest unoccupied molecular orbital; HOMO, highest occupied molecular orbital

Conjugated polymers	E_{onset}[A] [V]	E'_{onset}[B] [V]	I_{p}[C] (E_{HOMO}) [eV][D]	E_{g}[E] (bandgap energy) [eV][D]	E_{a}[F] (E_{LUMO}) [eV][D]
11a	0.38	0.57	5.18	2.37	2.81
11b	0.35	0.54	5.15	2.39	2.76

[A] Measured *v.* ferrocene/ferrocenium.

[B] $E'_{\mathrm{onset}} = E_{\mathrm{onset}} + 0.19\,\mathrm{eV}$ (measured *v.* Ag/AgCl).

[C] $I_{\mathrm{p}} = -(E'_{\mathrm{onset}} + 4.8)$.

[D] $1\,\mathrm{eV} = 96.5\,\mathrm{kJ\,mol^{-1}}$.

[E] E_{g}: the bandgap energy estimated from the onset wavelength of the UV-vis absorption and the equation $y = -0.033 \times x + 11.141$ ($x = \lambda_{\mathrm{onset}}$).

[F] $E_{\mathrm{a}} = I_{\mathrm{p}} + E_{\mathrm{g}}$.

Table 3. T_g values and thermal stability of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers 11a–11b (heating and cooling rate: 15°C)

Conjugated polymers	T_g[A] [°C]	T_1[B] [°C]	T_{10}[B] [°C]	Char yeild[C] [%]
11a	149	316	409	31
11b	150	309	386	39

[A] T_g: glass-temperature determined by the DSC method.

[B] T_1, T_{10}: temperature at which weight losses of 1 and 10%, respectively, were observed by TGA in N_2.

[C] Char yield at 800°C by TGA in N_2.

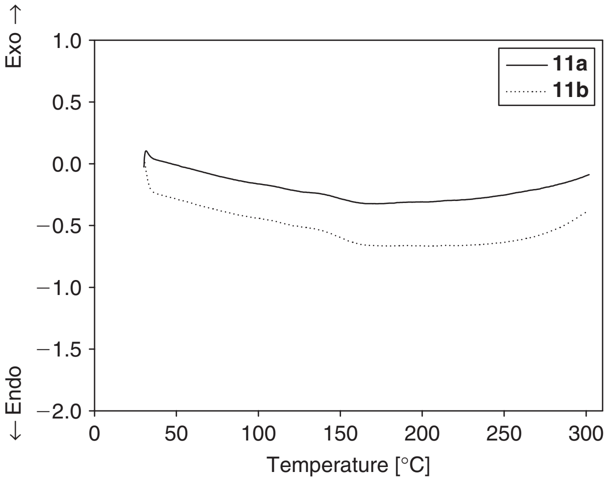


Fig. 5. DSC thermograms of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **11b**.

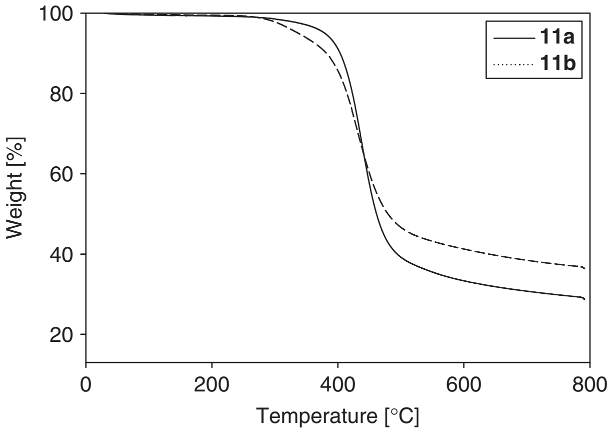


Fig. 6. TGA thermograms of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **11a** and **11b**.

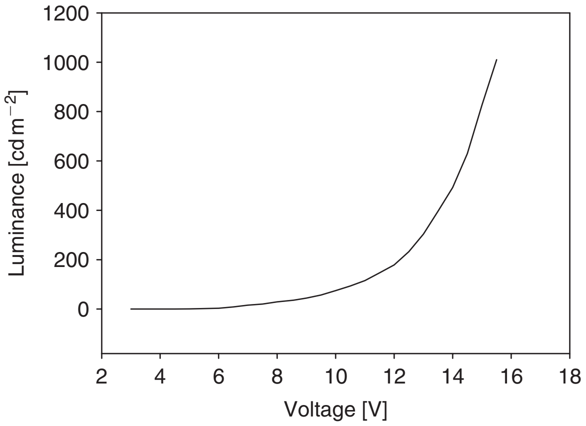


Fig. 7. *I–V* curves of ITO/PEDOT/**11b**/LiF.

as purchased. All reactions were carried out under nitrogen atmosphere and monitored by TLC analysis. Flash column chromatography was carried out on silica gel (230–400 mesh). Commercially available reagents were used without further purification unless otherwise noted. Ethyl acetate, dimethyl sulfoxide (DMSO), diisopropyl ether, hexanes, glacial acetic acid, methanol, and *p*-xylene were purchased from Mallinckrodt Chemical Co. Dry THF (reagent grade) and palladium 10 wt.-% on carbon were purchased from Aldrich. Benzoyl chloride, 1,4-hydroxybezene, DMAD, hydrazine hydrate, phosphorus oxychloride, and tetrabutylammonium bromide were purchased from Acros Chemical Co.

Analytical TLC was performed on pre-coated plates (silica gel 60 F-254) that were purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Purification by gravity column chromatography was carried out by use of Merck Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Infrared (IR) spectra were measured on a

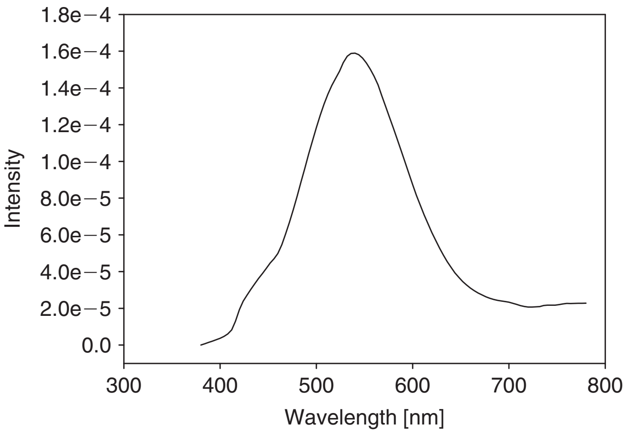


Fig. 8. EL spectrum of ITO/PEDOT/**11b**/LiF.

Bomem Michelson Series FT-IR spectrometer. The wavenumbers reported are referenced to the polystyrene (1601 cm^{-1}) absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. UV-Visible spectra were measured with a HP 8452A diode-array spectrophotometer. PL spectra were obtained on a Perkin–Elmer fluorescence spectrophotometer (LS 55). ^{1}H NMR spectra were obtained on a Bruker (300 MHz) spectrometer by use of [D$_6$]DMSO as solvent. ^{13}C NMR spectra were obtained on a Bruker (100 MHz) spectrometer with (D)chloroform as solvent. ^{13}C NMR chemical shifts are referenced to the centre of the CDCl$_3$ triplet (δ 77.0). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (Hertz). Elemental analyses were carried out on a Heraeus CHN-O RAPID element analyzer.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on a PGSTAT 20 electrochemical analyzer. The oxidation and reduction measurements were carried out in anhydrous CH$_2$Cl$_2$ and THF that contained 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte at a scan rate of 50 mV s^{-1}. The potentials were measured against an Ag/Ag$^+$ (0.01 M AgCl) reference electrode using ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.[42]

*Standard Procedure of 1-Phenyl-1*H*-Pyrazole Derivatives **2a** and **2b***[43]

A solution of sydnone (**1a** and **1b**, 0.031 mol, 1.0 mol equiv.) and DMAD (5.2 g, 0.037 mol, 1.2 mol equiv.) was dissolved and heated in *p*-xylene solution at reflux overnight. After the reaction was complete, the reaction mixture was concentrated under reduced pressure and precipitated by EtOH (15 mL). The resulting solution was cooled at −5°C for 4 h. The wet cake was filtered off and washed with cold EtOH (10 mL). The wet cake was then dried in a vacuum oven overnight to give the desired product **2a** and **2b** in 91–93% yield.

Dimethyl 1-phenyl-1*H*-pyrazole-3,4-dicarboxylate **2a**: δ_H ([D$_6$]DMSO, 300 MHz) 3.77 (s, 3H, OCH$_3$), 3.87 (s, 3H, OCH$_3$), 7.40–7.51 (m, 3H, ArH), 7.88–7.95 (m, 2H, ArH), 9.16 (s, 1H, pyrazole H).

Dimethyl 1-(4-methoxyphenyl)-1*H*-pyrazole-3,4-dicarboxylate **2b**: δ_H (CDCl$_3$, 300 MHz) 3.84 (s, 3H, OCH$_3$), 3.87 (s, 3H, OCH$_3$), 3.98 (s, 3H, OCH$_3$), 6.98 (d, 2H, *J* 9.0, ArH), 7.61 (d, 2H, *J* 9.0, ArH), 8.28 (s, 1H, pyrazole H). δ_C (CDCl$_3$, 75 MHz) 52.9, 53.5, 56.5, 115.5, 116.9, 122.7, 132.7, 133.2, 145.0, 160.4, 162.8, 163.0.

*Standard Procedure of 1-Phenyl-1*H*-Pyrazole-3,4-dicarbohydrazide Derivatives **3a** and **3b***[44]

A solution of 1-phenyl-1*H*-pyrazole derivatives (**2a** and **2b**, 1.0 mol equiv.) and hydrazine hydrate (excess amount, 4.0 mol equiv.) was heated in EtOH at reflux overnight. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and precipitated by EtOAc (15 mL). The resulting solution was cooled at −5°C for 4 h. The wet cake was filtered off and washed with cold EtOH (10 mL). The wet cake was dried in a vacuum oven overnight to give the desired product (**3a** and **3b**) in 74–76% yield.

1-Phenyl-1*H*-pyrazole-3,4-dicarbohydrazide **3a**: δ_H ([D$_6$]DMSO, 300 MHz) 4.56 (s, 2H, NH$_2$), 4.57 (s, 2H, NH$_2$), 4.72 (s, 2H, NH$_2$), 7.42 (d, 1H, *J* 7.12, ArH), 7.54 (t, 2H, *J* 7.32, ArH), 8.07 (d, 2H, *J* 7.90, ArH), 9.07 (s, 1H, pyrazole H), 10.35 (s, 1H, NH), 11.15 (s, 1H, NH). δ_C ([D$_6$]DMSO, 75 MHz) 119.27, 119.60, 128.14, 129.99, 133.17, 138.89, 141.94, 160.51, 161.43. ν_{max}/cm^{-1} (KBr) 3395 (br, NH), 1643 (m, C=O).

1-(4-Methoxyphenyl)-1*H*-pyrazole-3,4-dicarbohydrazide **3b**: δ_H ([D$_6$]DMSO, 300 MHz) 3.82 (s, 3H, OCH$_3$), 4.65 (s, 4H, NH$_2$), 4.71 (s, 2H, NH$_2$), 7.08 (d, 2H, *J* 9.0, ArH), 7.98 (d, 2H, *J* 9.0, ArH), 8.96 (s, 1H, pyrazole H), 10.32 (s, 1H, NH), 11.22 (s, 1H, NH). δ_C ([D$_6$]DMSO, 75 MHz) 55.9, 114.9, 118.9, 121.1, 132.4, 132.8, 141.4, 159.0, 160.6, 161.5.

*Standard Procedure of 1*H*-Pyrazole–Carbohydrazide Derivatives **5a** and **5b***[45]

A solution of 1-phenyl-1*H*-pyrazole-3,4-dicarbohydrazide (**3a** and **3b**, 0.80 g, 3.08 mmol equiv.) and pyridine (0.1 mol equiv.) in CH$_2$Cl$_2$ was stirred at room temperature for 10 min. 3-(4-Bromophenyl)acryloyl chloride **5** (1.58 g, 6.47 mmol equiv.) was added to the reaction mixture and stirred at room temperature for 8 h. After the reaction was complete, the reaction mixture was filtered and the solid washed with cool water (10 mL). The wet cake was dried in a vacuum oven overnight to give the desired product **5a** and **5b** in 73–78% yield.

*N*3′,*N*4′-Bis((*E*)-3-(4-bromophenyl)acryloyl)-1-phenyl-1*H*-pyrazole-3,4-dicarbohydrzide **5a**: White crystals, mp 297–299°C. δ_H ([D$_6$]DMSO, 300 MHz) 6.85 (d, 2H, *J* 9.0), 7.18–7.63 (m, 13H, ArH), 8.17 (d, 2H, *J* 9.0), 9.28 (s, 1H, pyrazole H), 10.79 (br, 4H, CONH). δ_C ([D$_6$]DMSO, 75 MHz) 110.7, 115.0, 118.7, 119.9, 120.2, 123.1, 123.4, 125.8, 130.1, 130.2, 132.4, 134.2, 134.7, 139.0, 139.4, 157.2, 158.3, 163.2, 165.0. ν_{max}/cm^{-1} (thin film, NaCl) 3212 (br, NH), 2921, 1620 (m, C=O), 1530, 1458, 1205, 1068, 1032, 969, 830, 811, 687. *m*/*z* (FAB) 681 (M + 4, 18), 679 (M + 2, 31), 677 (M, 16), 209 (100). (Found: C 51.2, H 3.3, N 12.2. Calc. for $C_{29}H_{22}Br_2N_6O_4$: C 51.4, H 3.3, N 12.4%.)

*N*3′,*N*4′-Bis((*E*)-3-(4-bromophenyl)acryloyl)-1-(4-methoxyphenyl)-1*H*-pyrazole-3,4-dicarbohydrazide **5b**: White crystals, mp 298–300°C. δ_H ([D$_6$]DMSO, 300 MHz) 3.79 (s, 3H, OCH$_3$), 6.78 (d, 2H, *J* 9.0), 7.07 (d, 2H, *J* 9.0, ArH), 7.44–7.59 (m, 13H, ArH), 8.00 (d, 2H, *J* 9.0), 9.08 (s, 1H, pyrazole H), 10.69 (br, 4H, CONH). δ_C ([D$_6$]DMSO, 75 MHz) 55.9, 115.0, 118.8, 121.5, 122.0, 126.1, 130.0, 131.9, 132.0, 134.3, 159.3, 160.0, 162.0, 164.7, 164.9. ν_{max}/cm^{-1} (thin film, NaCl) 3205 (br, NH), 2921, 1631 (m, C=O), 1535, 1487, 1257, 1205, 1070, 1030, 975, 835, 813, 729. *m*/*z* (FAB) 711 (M + 4, 26), 709 (M + 2, 42), 707 (M, 37), 209 (100). (Found: C 51.0, H 3.4, N 11.6. Calc. for $C_{30}H_{24}Br_2N_6O_5$: C 50.9, H 3.4, N 11.9%.)

*Standard Procedure of Preparation of 1*H*-Pyrazol-1,3,4-Oxadiazole Derivatives* ***6a*** *and* ***6b***[31]

A solution of 1*H*-pyrazole–carbohydrazide derivatives (**5a** and **5b**, 4.2 mmol, 1.0 mol equiv.) in $POCl_3$ (10 mL) was stirred at 90°C overnight. After the reaction was complete, the reaction mixture was added to cold water (10 mL) and neutralized with $NaHCO_3$ aqueous solution (10 mL) to precipitate the corresponding products. The crude product was filtered off and washed with cold water (5 mL). The wet cake was crystallized from EtOH and dried in a vacuum oven overnight to give the desired product **6a** and **6b** in 89–92% yield.

(*E*)-5,5′-(1-Phenyl-1*H*-pyrazole-3,4-diyl)bis(2-((*E*)-4-bromostyryl)-1,3,4-oxadiazole) **6a**: Yellow crystals, mp 229–231°C. δ_H ([D$_6$]DMSO, 300 MHz) 7.44–8.08 (m, 17H, HC=CH and ArH), 9.28 (s, 1H, pyrazole H). δ_C ([D$_6$]DMSO, 75 MHz) 108.3, 110.9, 111.0, 120.0, 123.7, 123.8, 128.9, 130.1, 130.2, 131.4, 131.9, 132.2, 132.5, 134.1, 136.1, 136.5, 138.2, 138.6, 138.8, 157.5, 157.7, 164.3, 164.8. ν_{max}/cm^{-1} (thin film, NaCl) 2922, 1636, 1602 (m, C=N), 1550, 1521, 1201, 1072, 1008, 962, 859, 808, 687. *m/z* (FAB) 645 (M + 4, 19), 643 (M + 2, 28), 641 (M, 19), 211 (100). (Found: C 54.1, H 2.9, N 12.8. Calc. for $C_{28}H_{18}Br_2N_6O_2$: C 54.2, H 2.8, N 13.1%.)

(*E*)-5,5′-(1-(4-Methoxyphenyl)-1*H*-pyrazole-3,4-diyl)bis(2-((*E*)-4-bromostyryl)-1,3,4-oxadiazole) **6b**: Yellow crystals, mp 262–264°C. δ_H ([D$_6$]DMSO, 300 MHz) 3.84 (s, 3H, OCH_3), 7.15–8.97 (m, 16H, HC=CH and Ar H), 9.60 (s, 1H, pyrazole H). δ_C ([D$_6$]DMSO, 75 MHz) 56.0, 108.7, 111.0, 115.2, 115.8, 119.2, 121.5, 121.7, 126.0, 129.9, 130.1, 130.3, 132.2, 134.1, 136.0, 136.4, 138.0, 138.2, 138.6, 157.6, 158.5, 159.6, 164.8, 165.3. ν_{max}/cm^{-1} (thin film, NaCl) 2925, 1643, 1605 (m, C=N), 1516, 1248, 1203, 1068, 1005, 960, 835, 809. *m/z* (FAB) 675 (M + 4, 25), 673 (M + 2, 42), 671 (M, 29), 391 (100). (Found: C 53.4, H 3.0, N 12.5. Calc. for $C_{30}H_{20}Br_2N_6O_3$: C 53.6, H 3.0, N 12.5%.)

1,4-Bis(dodecyloxy)benzene ***8***[36]

Mp 70–71°C. δ_H ($CDCl_3$, 300 MHz) 0.86–2.01 (t, 6H, *J* 6.0), 1.27–1.44 (m, 36H), 1.70–1.79 (m, 4H), 3.87–3.92 (t, 4H, *J* 7.5), 6.82 (s, 4H).

1,4-Dibromo-2,5-bis(dodecyloxy)benzene ***9***[36]

Mp 77–78°C. δ_H ($CDCl_3$, 300 MHz) 0.80–0.83 (t, 6H, *J* 4.5), 1.20–1.41 (m, 36H), 1.70–1.77 (m, 4H), 3.85–3.90 (t, 4H, *J* 7.5), 7.01 (s, 2H). δ_C ([D$_6$]DMSO, 75 MHz) 14.1, 22.5, 25.9, 29.0, 29.3, 29.5, 31.9, 70.2, 111.1, 118.4, 150.0. (Found: C 58.6, H 8.7. Calc. for $C_{30}H_{52}Br_2O_2$: C 59.6, H 8.7%.)

1,4-Bis(dodecyloxy)-2,5-divinylbenzene ***10***[36]

Mp 62–63°C. δ_H ($CDCl_3$, 300 MHz) 0.87–0.90 (t, 6H, *J* 4.1), 1.27–1.36 (m, 32H), 1.20–1.41 (m, 36H), 1.45–1.49 (m, 4H), 1.77–1.81 (m, 4H), 5.24–5.27 (dd, 2H, *J* 5.9 and 0.8), 5.71–5.75 (dd, 2H, *J* 9.8 and 0.8), 6.99 (s, 2H), 7.02–7.07 (dd, 2H, *J* 6.7 and 4.0). (Found: C 81.9, H 11.8. Calc. for $C_{34}H_{58}O_2$: C 81.9, H 11.8%.)

*Standard Procedure of the Preparation of 1*H*-Pyrazol-1,3,4-Oxadiazole Derivatives* ***11a*** *and* ***11b***[37]

To a solution of 1,4-bis(dodecyloxy)-2,5-divinylbenzene **10** (0.1 g, 0.2 mmol, 1.0 equiv.), Pd(PPh_3)$_4$, and a few crystals of 2,6-di-*tert*-butyl-4-methylphenol in DMAc (6 mL) and triethylamine (3 mL) was added (*E*)-5,5′-(1-phenyl-1*H*-pyrazole-3,4-diyl)bis(2-((*E*)-4-bromostyryl)-1,3,4-oxadiazole) **6a** (0.23 mmol, 1.1 equiv.) or (*E*)-5,5′-(1-(4-methoxyphenyl)-1*H*-pyrazole-3,4-diyl)bis(2-((*E*)-4-bromostyryl)-1,3,4-oxadiazole) **6b** (0.23 mmol, 1.1 equiv.). The resulting solution was heated at 130°C for 50 h in N_2. After the reaction was complete, the reaction mixture was filtered and added to MeOH (150 mL) to precipitate the crude product in 63–71% yield. For further purification, the crude product was dissolved in hot DMF. The resulting hot solution was quickly filtered through Celite to remove Pd catalyst and washed with hot DMF (3 mL). The filtrates were added to cold MeOH (5 mL). The resulting precipitate was filtered off, crystallized from DMF, and dried in a vacuum oven overnight to give the desired product **11a** and **11b** as a yellow solid in 48–53% yield.

Poly(2-(3-(5-(4-(2,5-bis(dodecyloxy)-4-((*E*)-prop-1-enyl)styryl)styryl)-1,3,4-oxadiazol-2-yl)-1-phenyl-1*H*-pyrazol-4-yl)-5-styryl-1,3,4-oxadiazole) **11a**. δ_H ($CDCl_3$, 300 MHz) 0.79–1.78 (m, 46H), 3.86–3.94 (m, 4H, OCH_2), 6.78–7.82 (m, 8H, HC=CH and 15H, ArH), 8.72 (s, 1H, pyrazole H). ν_{max}/cm^{-1} (thin film, NaCl) 2923, 2853, 1636, 1597 (m, C=N), 1497, 1460, 1379, 1250, 1204, 1066, 964, 905, 862, 832. (Found: C 76.2, H 7.9, N 8.4. Calc. for $C_{65}H_{80}N_6O_4$: C 77.3, H 8.0, N 8.3%.)

Poly(2-(3-(5-(4-(2,5-bis(dodecyloxy)-4-((*E*)-prop-1-enyl)styryl)styryl)-1,3,4-oxadiazol-2-yl)-1-(4-methoxyphenyl)-1*H*-pyrazol-4-yl)-5-styryl-1,3,4-oxadiazole) **11b**. δ_H ($CDCl_3$, 300 MHz) 0.80–1.88 (m, 46H), 3.82–4.03 (m, 4H, OCH_2), 6.74–7.79 (m, 8H, HC=CH and 14H, ArH), 8.61 (s, 1H, pyrazole H). ν_{max}/cm^{-1} (thin film, NaCl) 2970, 2921, 1738, 1610, 1595 (m, C=N), 1518, 1420, 1365, 1205, 1066, 964, 897, 831, 809. (Found: C 75.5, H 7.8, N 8.2. Calc. for $C_{66}H_{82}N_6O_5$: C 76.3, H 8.0, N 8.1%.)

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