www.publish.csiro.au/journals/ajc

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

En-Ming Chang,^B Shin-Lin Huang,^C Cheng-Tien Lee,^B Hui-Chang Lin,^A Chun-Yen Chen,^B Yu-Ying Huang,^A Shao-Kai Lin,^C and Fung Fuh Wong^{A,D}

^AGraduate Institute of Pharmaceutical Chemistry, China Medical University, Taichung, Taiwan 40402, Republic of China.

^BDepartment of Chemistry, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China.

^CSustainable Environment Research Center, National Cheng Kung University, Tainan City, Taiwan 709, Republic of China.

^DCorresponding author. Email: wongfungfuh@yahoo.com.tw

New soluble poly(*p*-phenylenevinylene) derivatives with 1,3,4-oxadiazole and pyrazole rings along the main chain were synthesized by Heck coupling. The new conjugated polymers are soluble in common organic solvents as a result of the fully conjugated backbone with dodecyloxy side groups. The polymers show relatively high glass-transition temperatures (up to 160° C) and good satisfactory thermal stability. Solutions of the polymers emit blue-greenish light with photoluminescence (PL) emission maxima around 490–500 nm. The PL spectrum of the polymer's thin films, with a maximum at 515 nm, shows a red-shift (~20 nm), with respect to the solution spectrum. Cyclic voltammetry reveals that both conjugated polymers have reversible oxidation and irreversible reduction, making them n-type electroluminescent materials. The electron affinity of the new polymers was estimated as 2.73–2.74 eV. The weight-average molecular weights (M_w) of the new soluble polymers were in the range of 4790–4950.

Manuscript received: 12 August 2008. Manuscript accepted: 10 February 2009.

Introduction

Soluble π -conjugated electroluminescent polymers have attracted much attention as the active component in lightemitting diodes,^[1-4] solid-state lasers,^[5,6] and transistors after the discovery of light emission from poly(*p*-phenylenevinylene) (PPV).^[7–10] Typically, conjugated polymers such as PPV, poly(thiophene) (PT), and their derivatives tend to p-type, that is, they favour hole transport.^[11,12] The recent interest in soluble π -conjugated polymers with good electron-injection capability was enthusiastically investigated, particularly in the conjugated polymers that contain electron-withdrawing units in the main chain or at side groups to improve electron-transport capability.^[13–15]

In a previous study, we demonstrated that multiple 1,3,4oxadiazole units can promote thermal stability and electroluminescent properties when they are introduced into the conjugated main core of pyrazole derivatives.^[16] As a result, aromatic multiple 1,3,4-oxadiazole-based conjugated polymers have been developed as promising candidates for light-emitting devices because of their thermal, hydrolytic, and photo-stability,^[17–20] electron affinity, and hole blocking ability in this work.^[12,21,22] 1,3,4-Oxadiazole-based heterocyclic conjugated polymers have also been enthusiastically investigated to improve electron injection, transport properties, and confer rigidity, for example, 1,3,4oxadiazole–carbazole,^[23] and 1,3,4-oxadiazole–pyridine.^[24]



Fig. 1. The new soluble poly(*p*-phenylenevinylene) derivatives with 1,3,4-oxadiazole and pyrazole rings along the main chain.

Because the chromophore pyrazole can play an assistant role in controlling the fundamental electroluminescent process, 1,3,4-oxadiazole-based pyrazole derivatives are revealed as efficient blue-greenish electroluminescent materials.^[16] As a result, we established the introduction of pyrazole and multiple 1,3,4-oxadiazole units into the conjugated polymer's main chain to improve the electron-transporting properties. This new soluble PPV-based conjugated polymer with 1,3,4-oxadiazole and pyrazole rings in the backbone (Fig. 1) was successfully



synthesized by 1,3-dipolar addition, $^{[16]}$ dehydration, $^{[25]}$ and Heck coupling. $^{[16]}$

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,5b**). Sydnone compounds (**1a,1b**) were prepared by following the literature procedure developed in our laboratory.^[26] Sydnone compounds (**1a,1b**) with various substituents in the *N*1-phenyl ring, 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,2b**) as a white solid in almost quantitative yield (91–93%).

This 1,3-dipolar cyclization has proved to be an efficient and economical way to generate pyrazole derivatives. Treating 1-aryl-1*H*-pyrazole-3,4-dicarboxylate (**2a,2b**) with hydrazine hydrate at reflux afforded the corresponding dihydrazide product (**3a,3b**) in good yield (74–76%) according to published reports.^[27] Dihydrazide compounds (**3a,3b**) reacted with benzoyl chloride in CH₂Cl₂ at room temperature for 2 to 3 h to give the corresponding bis(trihydrazide) products (**4a,4b**) in 78–83% yields. These compounds (**4a,4b**) were dehydration cyclized to form the 1,3,4-oxadiazole-based pyrazole derivatives (**5a,5b**) in 90–92% yield in the presence of POCl₃.^[25]

The synthetic route of 1,4-didodecyloxy-2,5-divinylbezene **9** is outlined in Scheme 2. 1,4-Dibromo-2,5-didodecyloxybezene **8** was easily synthesized in two steps with a total yield of 64% using 1,4-hydroxybezene **6** as starting material following the



Scheme 3.

Table 1. Characterization of the soluble 1,3,4-oxadiazole-based conjugated polymers 10a and 10b

Conjugated polymer	GPC		Absorbance λ_{max} (UV-vis) [nm]			Emission λ_{max} (PL) [nm]		
	M _n [kDa]	Pd	CH_2Cl_2	Toluene	Film	CH_2Cl_2	Toluene	Film
10a	4949	2.04	306, 404	300, 393	302, 408	498	493	515
10b	4790	2.94	308, 415	300, 400	303, 410	499	492	513

previously reported procedure.^[28] Eventually, the Stille coupling of 1,4-dibromo-2,5-didodecyloxybezene **8** with 2.2 equiv. of vinyltin reagent was performed to give the coupled product 1,4-didodecyloxy-2,5-divinylbezene **9** in good yield (73%).^[29]

Soluble 1,3,4-oxadiazole-pyrazole conjugated polymers (10a,10b) were synthesized by the Pd-catalyzed Heck coupling reaction of 1,3,4-oxadiazole-based pyrazole derivatives 5a,5b with divinyl compound 9 in 48-53% yield (see Scheme 3).^[30] The two polymers are soluble in common organic solvents such as chloroform, dichloromethane, N,N-dimethylformamide (DMF), toluene, tetrahydrofuran (THF), and xylene, etc. They are all yellow-coloured wool-like solids. Structural characterization of the polymers was accomplished by FT-IR, ¹³C NMR, and ¹H NMR spectroscopy, and elemental analysis. The weight-average molecular weights (M_n) of the new synthetic polymers, as determined by gel permeation chromatography using polystyrene as a standard, were in the range of 4790-4950 (see Table 1). According to the presence of the dodecyloxy side chain^[31] and the Heck coupling polymerization,^[32] relatively low molecular weight copolymers were provided. The results are consistent with the reported literature data.[32,33]

Optical Properties

The new soluble 1,3,4-oxadiazole–pyrazole conjugated polymers (**10a,10b**) exhibit very similar absorption spectra as shown in Table 1 and Figs 2 and 3. They all show two main strong absorption peaks: one in the visible range at \sim 403 nm and the



Fig. 2. The UV-vis and PL spectra of 10a and 10b in CH_2Cl_2 solution.

other in the UV region at 305 nm. Compared with that of poly (*p*-phenylenevinylene) that contains 1,3,4-oxadiazole (OX1-PPV, the λ_{max} values are 328 and 393 nm in THF solution or in a thin film, respectively),^[24] the UV absorption peak of the new polymers (**10a,10b**) is blue-shifted by 23 nm, whereas the visible absorption peak is red-shifted by 10 nm. The absorption at 305 nm can be assigned to the π - π * transition of the cross-conjugated oxadiazole segment, which is confirmed by the same



Fig. 3. The UV-vis and PL spectra of 10a and 10b in a thin film.

absorption maximums of the monomer (**5a**,**5b**).^[16] The identical absorption maximums of the oxadiazole units before and after the polymerization imply that, in dilute solution, the electronic interactions between the oxadiazole units and the PPV backbone are rather limited.^[23] 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.

Figs 2 and 3 show the photoluminescence (PL) spectra of the new soluble 1,3,4-oxadiazole–pyrazole conjugated polymers (**10a,10b**). The polymer exhibits a maximum emission at 500 nm in organic solvent or the thin film, and this emission maximum is clearly independent of the excitation wavelengths. Emissions of the 1,3,4-oxadiazole–pyrazole hybrids^[16] at 365–375 nm and the 1,3,4-oxadiazole unit at 395 nm are not observed.^[24] However, the absorption spectra of the new polymers show almost identical maximums to their absorption spectra, which indicates the existence of efficient energy transfer from the oxadiazole moiety to the PPV backbone.

Cyclic Voltammetry Measurements

The electrochemical properties of the new soluble 1,3,4oxadiazole–pyrazole conjugated polymers (**10a,10b**) were investigated by cyclic voltammetry, as shown in Figs 4 and 5, and the resulting data are summarized in Table 2. Upon the anodic sweep, **10a** and **10b** show reversible oxidation processes and irreversible reduction. Compounds **10a** and **10b** were used as examples and are shown in Figs 4 and 5. The bandgap energies of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers (**10a,10b**) are estimated from the onset wavelength (λ_{onset}) of the UV-vis absorption.^[12] Compounds **10a,10b** have high lowest unoccupied molecular orbital values of ~2.73 eV and high electron affinities of ~2.43 eV.

Thermal Properties

Thermal and thermomechanical characterization of the polymers was carried out by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass-transition temperatures (T_g s) 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 (see Table 3 and Fig. 6). Compound **10a** showed a slightly lower T_g (164°C)



Fig. 4. Cyclic voltammetry of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers of 10a.



Fig. 5. Cyclic voltammetry of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers of 10b.

than **10b** (167°C), which was attributed to the presence of the *para*-methoxy withdrawing group in the *N*1-phenyl ring. The TGA thermograms of the polymers are summarized in Table 3 and Fig. 7. The soluble 1,3,4-oxadiazole–pyrazole conjugated polymers (**10a**,**10b**) were stable up to \sim 250–260°C in N₂. They afforded a relatively low anaerobic char yield (\sim 35%) at 800°C because of the thermally sensitive alkoxy side groups. Compound **10b** was slightly more thermally stable than **10a**, and all its thermal properties were superior to PPV.

Electroluminescent Properties

A double-layer organic light-emitting diode device with a structure of indium tin-oxide (ITO)/polythiophene/1,3,4-oxadiazole– pyrazole conjugated polymers (**10a**)/LiF was 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 a blue-greenish emission at 5.9 V onset voltage (see Fig. 8). The red-shifted electroluminescence maximum of the device at 503 nm (see Fig. 9) was observed with a PL maximum at 515 nm in the film.

Conclusions

Two new soluble polymers that contain 1,3,4-oxadiazole and pyrazole rings along the main chain have been synthesized by Heck coupling. The polymers are readily soluble in common organic solvents and had moderate T_g (164 and 167°C) and have a good satisfactory thermal stability. Compound **10a** has a lower T_g and a higher electron affinity than **10b**. The electron affinity of the new polymers was estimated as 2.73–2.74 eV. The new

Fable 2.	Electrochemical properties of soluble 1,3,4-oxadiazole-pyrazole conjugated polymers 10a and 10b
	HOMO, highest occupied molecular orbitals; LUMO, lowest unoccupied molecular orbital

Conjugated polymers	$E_{\text{onset}}^{\text{A}}$ [V]	$E'_{\text{onset}}^{\text{B}}$ [V]	$I_p^{C,D} E_{HOMO} [eV]$	$E_{g}^{D,E}$ bandgap energy [eV]	$E_{a}^{F} E_{LUMO} [eV]$
10a	0.41	0.60	5.21	2.47	2.74
10b	0.36	0.55	5.16	2.43	2.73

^AMeasured versus ferrocene/ferrocenium.

 ${}^{\mathrm{B}}E'_{\mathrm{onset}} = E_{\mathrm{onset}} + 0.19 \,\mathrm{eV}$ (measured versus Ag/AgCl).

 $^{\rm C}I_{\rm p} = -(E'_{\rm onset} + 4.8).$

 $^{\rm D}1\,{\rm eV} = 96.5\,{\rm kJ\,mol^{-1}}$

^E E_g , the bandgap energy estimated from the onset wavelength of UV-vis absorption and the equation $Y = -0.033 \times X + 11.141 \ (X = \lambda_{onset})$. ^F $E_a = I_p + E_g$.

Table 3. T_g values and thermal stability of soluble 1,3,4-oxadiazolepyrazole conjugated polymers 10a and 10b (heating and cooling rate: 15° C min⁻¹)

Conjugated polymers	$T_{g}^{A} [^{\circ}C]$	In N ₂			
		$T_1{}^{\rm B} \ [^{\circ}{\rm C}]$	$T_{10}^{\rm B} [^{\circ}{\rm C}]$	Y_{c}^{C} [%]	
10a	164	264	389	34	
10b	168	257	346	36	

 ${}^{A}T_{g}$, glass-temperature determined by the differential scanning calorimetry method.

 ${}^{\mathrm{B}}T_1$, T_{10} , temperature at which weight losses of 1 and 10%, respectively, were observed by thermogravimetric analysis.

 $^{C}Y_{c}$, char yield at 800°C by TGA.



Fig. 6. Differential scanning calorimetry thermograms of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers 10a and 10b.



Fig. 7. Thermogravimetric analysis thermograms of soluble 1,3,4-oxadiazole–pyrazole conjugated polymers **10a** and **10b**.



Fig. 8. I-V curves of ITO/PEDOT/10a/LiF.



Fig. 9. EL spectrum of ITO/PEDOT/10a/LiF.

conjugated polymers are soluble in common organic solvents according to the fully conjugated backbone with solubilizing dedecyloxy side groups. The polymers were luminescent with PL emission maxima around 490–515 nm in solution or in a thin film. Cyclic voltammetry displayed that both conjugated polymers had reversible reduction and irreversible oxidation, making them n-type electroluminescent materials. The weight-average molecular weights (M_w) of the new soluble polymers were in the range of 4790–4950.

Experimental

General Procedure

Sydnones were synthesized according to literature procedures.^[26] All chemicals were reagent grade and used

as purchased. All reactions were carried out under a 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, diisopropyl ether, hexanes, glacid acetic acid, methanol, and *p*-xylene were purchased from Mallinckrodt Chemical Co. Dry THF (reagent grade) and 10 wt.-% palladium on carbon were purchased from Aldrich. Benzoyl chloride, 1,4dihydroxybenzene, dimethyl acetylenedicaboxylate, hydrazine hydrate, phosphorus oxychloride, and tetrabutylammonium bromide were purchased from Acros Chemical Co.

Analytical TLC was performed on precoated plates (silica gel 60 F-254) 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 Bomem Michelson Series FT-IR spectrometer. The wavenumbers reported are referenced to the polystyrene absorption at 1601 cm⁻¹. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. UV-Vis spectra were measured with a HP 8452A diode-array spectrophotometer. PL spectra were obtained on a Perkin-Elmer fluorescence spectrophotometer (LS 55). Proton NMR spectra were obtained on a Bruker (300 MHz) spectrometer by use of (D₆)DMSO as solvent. Carbon-13 NMR spectra were obtained on a Bruker (100 MHz) spectrometer by use of D-chloroform as solvent. Carbon-13 chemical shifts are referenced to the centre of the CDCl₃ 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 Measurements

Cyclic voltammetry and differential pulse voltammetry measurements were performed on a PGSTAT 20 electrochemical analyzer. The oxidation and reduction measurements were carried out, in anhydrous CH_2Cl_2 and THF that contained 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 50 mV s⁻¹. The potentials were measured against a 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.^[34]

Standard Synthesis Procedure of 1-Phenyl-1H-pyrazole Derivatives **2a** and **2b**

A solution of sydnone (**1a** and **1b**, 0.031 mol, 1.0 mol equiv.) and dimethyl acetylenedicaboxylate (5.2 g, 0.037 mol, 1.2 mol equiv.) was dissolved and heated in a *p*-xylene solution at reflux overnight. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and precipated 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 3.77 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃), 7.40–7.51 (m, 3H, Ar-H), 7.88–7.95 (m, 2H, Ar-H), 9.16 (s, 1H, pyrazole-H).

Dimethyl 1-(4-Methoxyphenyl)-1H-pyrazole-3,4dicarboxylate (**2b**)

 $δ_{\rm H}$ 3.84 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃), 3.98 (s, 3H, OCH₃), 6.98 (d, 2H, *J* 9.0, Ar-H), 7.61 (d, 2H, *J* 9.0, Ar-H), 8.28 (s, 1H, pyrazole-H). $δ_{\rm C}$ 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 Synthesis Procedure of 1-Phenyl-1H-pyrazole-3,4-dicarbohydrazide Derivatives **3a** and **3b**^[27]

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 solution at reflux overnight. After the reaction was complete, 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 then dried in a vacuum oven overnight to give the desired product (**3a** and **3b**) in 74–76% yield.

1-Phenyl-1H-pyrazole-3,4-dicarbohydrazide (3a)

 $δ_{\rm H}$ 4.56 (s, 2H, NH₂), 4.57 (s, 2H, NH₂), 4.72 (s, 2H, NH₂), 7.42 (d, 1H, *J* 7.12, Ar-H), 7.54 (t, 2H, *J* 7.32, Ar-H), 8.07 (d, 2H, *J* 7.90, Ar-H), 9.07 (s, 1H, pyrazole-H), 10.35 (s, 1H, NH), 11.15 (s, 1H, NH). $δ_{\rm C}$ ((D₆)DMSO) 119.27, 119.60, 128.14, 129.99, 133.17, 138.89, 141.94, 160.51, 161.43. $ν_{\rm max}$ (KBr)/cm⁻¹ 3395 (br, NH), 1643 (m, C=O).

1-(4-Methoxyphenyl)-1H-pyrazole-3,4dicarbohydrazide (**3b**)

 $δ_{\rm H}$ 3.82 (s, 3H, OCH₃), 4.65 (s, 4H, NH₂), 4.71 (s, 2H, NH₂), 7.08 (d, 2H, *J* 9.0, Ar-H), 7.98 (d, 2H, *J* 9.0, Ar-H), 8.96 (s, 1H, pyrazole-H), 10.32 (s, 1H, NH), 11.22 (s, 1H, NH). $δ_{\rm C}$ ((D₆)DMSO) 55.9, 114.9, 118.9, 121.1, 132.4, 132.8, 141.4, 159.0, 160.6, 161.5.

Standard Synthesis Procedure of 1H-Pyrazolecarbohydrazide Derivatives **4a** and **4b**

A solution of 1-phenyl-1*H*-pyrazole-3,4-dicarbohydrazide (**3a**,3**b**, 2.0 g, 1.0 mol equiv.) and pyridine (0.1 mol equiv.) was stirred in CH₂Cl₂ at room temperature for 10 min. Benzoyl chloride (2.7 g, 2.5 mol 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 obtained washed with cool water (10 mL). The wet cake was dried in a vacuum oven overnight to give the desired product (**4a**,**4b**) in 78–83% yield.

N3',N4'-Bis(4-bromophenyl)-1-phenyl-1H-pyrazole-3,4-dicarbohydrazide (**4a**)

Mp 311–313°C. $\delta_{\rm H}$ 7.12 (d, 2H, Ar-H), 7.45–8.21 (m, 11H, Ar-H), 9.15 (s, 1H, pyrazole-H), 10.72 (br, 4H, NH), 10.79 (s, 1H, NH), 11.32 (s, 1H, NH), 11.92 (s, 1H, NH). $\delta_{\rm C}$ ((D₆)DMSO) 115.8, 118.3, 120.6, 120.7, 123.4, 127.4, 127.5, 130.8, 131.1, 132.4, 135.8, 159.1, 159.7, 165.0, 165.3. $\nu_{\rm max}$ (thin film, NaCl)/cm⁻¹ 3208 (b, NH), 1631 (m, C=O), 1520, 1473, 1261, 1111, 1010, 839, 763, 738, 691. *m*/*z* (FABMS) 629 (24%) [M + 2], 627 (49) [M + 1], 626 (25) [M], 191 (100). (Found: C 47.98, H 2.94, N 13.39. Calc. for C₂₅H₁₈Br₂N₆O₄: C 47.95, H 2.90, N 13.42%.)

N3',N4'-Bis(4-bromobenzoyl)-1-(4-methoxyphenyl)-1H-pyrazole-3,4-dicarbohydrazide (**4b**)

Mp 316–318°C. $\delta_{\rm H}$ 3.80 (s, 3H, OCH₃), 7.08 (d, 2H, J 9.0, Ar-H), 7.58–8.02 (m, 8H, Ar-H), 8.10 (d, 2H, J 9.0, Ar-H), 9.09 (s, 1H, pyrazole-H), 10.84 (br, 4H, NH), 10.72 (s, 1H, NH), 11.14 (s, 1H, NH), 11.90 (s, 1H, NH). $\delta_{\rm C}$ ((D₆)DMSO) 55.9, 115.0, 118.8, 121.5, 126.0, 126.1, 130.0, 131.9, 132.0, 132.3, 134.4, 159.3, 160.0, 162.0, 164.7, 164.9. $\nu_{\rm max}$ (thin film, NaCl)/cm⁻¹ 3208 (b, NH), 1620 (m, C=O), 1448, 1258, 1174, 1066, 1009, 965, 831, 743, 708. *m*/*z* (FABMS) 659 (19%) [M + 2], 657 (35) [M + 1], 656 (20) [M], 183 (100). (Found: C 47.54, H 3.06, N 12.82. Calc. for C₂₆H₂₀Br₂N₆O₅: C 47.58, H 3.07, N 12.81%.)

Standard Synthetic Procedure of the Preparation of 1H-Pyrazol-1,3,4-oxadiazole Derivatives **5a** and **5b**^[25]

A solution of 1H-pyrazole-carbohydrazide derivatives (**4a**,**4b**, 4.2 mmol, 1.0 mol equiv.) in POCl₃ (10 mL) was stirred at 90°C for overnight. After the reaction was complete, the reaction mixture was added to cold water (10 mL) and neutralized with a NaHCO₃ 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 (**5a**,**5b**) in 90–92% yield.

5,5'-(1-Phenyl-1H-pyrazole-3,4-diyl)bis(2-(4-bromophenyl)-1,3,4-oxadiazole) (**5a**)

Mp 238–240°C. $\delta_{\rm H}$ 7.49–8.09 (m, 13H, Ar-H), 9.66 (s, 1H, pyrazole-H). $\delta_{\rm C}$ ((D₆)DMSO) 118.5, 118.7, 120.1, 124.5, 124.8, 127.6, 130.5, 131.3, 131.4, 133.9, 134.2, 135.0, 138.5, 138.7, 157.3, 157.7, 163.9, 164.3. $\nu_{\rm max}$ (thin film, NaCl)/cm⁻¹ 3208 (b, NH), 1610, 1597, 1530, 1496, 1479, 1226, 1069, 1010, 964, 832, 757, 688. *m*/*z* (FABMS) 593 (39%) [M+2], 592 (60) [M+1], 591 (38) [M], 289 (100). (Found: C 50.85, H 2.40, N 14.21. Calc. for C₂₅H₁₄Br₂N₆O₂: C 50.87, H 2.39, N 14.24%.)

2-Phenyl-5-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)-1-p-tolyl-1H-pyrazol-3-yl)-1,3,4-oxadiazole (**5b**)

Mp 238–400°C. $\delta_{\rm H}$ 7.49–8.09 (m, 13H, Ar-H), 9.66 (s, 1H, pyrazole-H). $\delta_{\rm C}$ ((D₆)DMSO) 109.4, 118.5, 118.7, 120.1, 124.5, 124.8, 127.6, 130.5, 161.3, 131.4, 133.9, 134.2, 135.0, 138.5, 138.7, 157.3, 157.7, 163.9, 164.3. $\nu_{\rm max}$ (thin film, NaCl)/cm⁻¹ 1610, 1597, 1530, 1496, 1479, 1233, 1069, 1010, 964, 832, 757, 688. *m*/*z* (FABMS) 593 (38) [M+2], 592 (59) [M+1], 590 (38) [M], 289 (100). (Found: C 50.85, H 2.40, N 14.20. Calc. for C₂₅H₁₄Br₂N₆O₂: C 50.87, H 2.39, N 14.24%.)

1,4-Bis(dodecyloxy)benzene (7)^[28]

Mp 70–71°C. $\delta_{\rm H}$ (CDCl₃) 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).

11,4-Dibromo-2,5-bis(dodecyloxy)benzene (8)^[28]

Mp 77–78°C. $\delta_{\rm H}$ (CDCl₃) 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). $\delta_{\rm C}$ ((D₆)DMSO) 14.1, 22.5, 25.9, 29.0, 29.3, 29.5, 31.9, 70.2, 111.1, 118.4, 150.0. (Found: C 58.63, H 8.72. Calc. for C₃₀H₅₂Br₂O₂: C 59.59, H 8.69%.)

1,4-Bis(dodecyloxy)-2,5-divinylbenzene (9)^[28]

Mp 62–63°C. $\delta_{\rm H}$ (CDCl₃) 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 81.90, H 11.83. Calc. for C₃₄H₅₈O₂: C 81.85, H 11.77%.)

Standard Synthetic Procedure for the Preparation of 1H-Pyrazol-1,3,4-oxadiazole Derivatives **10a** and **10b**^[29]

A solution of 1,4-bis(dodecyloxy)-2,5-divinylbenzene (9, 0.1 g, 0.2 mmol, 1.0 equiv.), Pd(PPh₃)₄, and a few crystals 2,6,-ditert-butyl-4-methylphenol in 6 mL of DMAc and 3 mL of triethylamine was added 5,5'-(1-phenyl-1H-pyrazole-3,4-diyl)bis (2-(4-bromophenyl)-1,3,4-oxadiazole) (5a, 0.21 mmol, 1.1 equiv.). The resulting solution was heated at 130°C for 50 h in N₂. After the reaction was complete, the reaction mixture was filtrated and MeOH (150 mL) added to precipitate the crude product in 63-72% yield. For further purification, the crude product was dissolved in hot DMF. The hot resulting solution was quickly filtered through Celite to remove the Pd catalyst and washed with hot DMF (3 mL). The filtrates were added to cold MeOH (5 mL). The resulting precipitate was filtered, crystallized from DMF, and dried in a vacuum oven overnight to give the desired product 10a and 10b as a yellow solid in 48-53% vield.

Poly(2-(3-(5-(4-(2,5-bis(dodecyloxy)-4-((E)-prop-1enyl)styryl)phenyl)-1,3,4-oxadiazol-2-yl)-1-phenyl-1Hpyrazol-4-yl)-5-phenyl-1,3,4-oxadiazole) (**10a**)

 $δ_{\rm H}$ (CDCl₃) 0.90–1.74 (m, 46H), 3.78–3.95 (m, 4H, OCH₂), 6.73–8.23 (m, 19H, Ar-H and HC=CH), 8.75 (s, 1H, pyrazole-H). $ν_{\rm max}$ (thin film, NaCl)/cm⁻¹ 2920, 2851, 1656, 1598, 1492, 1258, 1202, 1049, 965, 892, 833. (Found: C 75.98, H 7.87, N 8.57. Calc. for C₆₁H₇₆N₆O₄: C 76.53, H 8.00, N 8.78%.)

Poly(2-(3-(5-(4-(2,5-bis(dodecyloxy)-4-((E)-prop-1-enyl)styryl)phenyl)-1,3,4-oxadiazol-2-yl)-1-(4methoxyphenyl)-1H-pyrazol-4-yl)-5-phenyl-1,3,4-oxadiazole) (**10b**)

 $\delta_{\rm H}$ (CDCl₃) 0.79–1.77 (m, 46H), 3.80–3.97 (m, 4H, OCH₂), 3.89 (s, 3H, OCH₃), 6.88–8.12 (m, 18H, Ar-H and HC=CH), 8.65 (s, 1H, pyrazole-H). ν_{max} (thin film, NaCl)/cm⁻¹ 2923, 1670, 1596, 1510, 1496, 1394, 1250, 1205, 1067, 965, 892, 831. (Found: C 73.87, H 7.52, N 8.40. Calc. for C₆₂H₇₈N₆O₅: C 76.42, H 7.96, N 8.51%.)

Acknowledgements

We are grateful the National Science Council of Republic of China for financial support. We also appreciate Professor Mou-Yung Yeh for his illuminating discussion and helpful assistance in preparing this manuscript.

References

- R. H. Friend, R. M. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradly, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* 1999, 397, 121. doi:10.1038/16393
- [2] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed. Engl.* 1998, 37, 402. doi:10.1002/(SICI)1521-3773(19980302)37:4<402:: AID-ANIE402>3.0.CO;2-9
- [3] A. Greiner, Polym. Adv. Technol. 1998, 9, 371. doi:10.1002/(SICI)1099-1581(199807)9:7<371::AID-PAT817>3.0.CO;2-7
- [4] W. J. Feast, J. Tssibouklis, K. L. Pouwer, L. Groenendaal, E. W. Meijer, *Polymer* 1996, 37, 5017. doi:10.1016/0032-3861(96)00439-9
- [5] F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, A. J. Heeger, Acc. Chem. Res. 1997, 30, 430. doi:10.1021/AR9501910

- [6] C. Zenz, W. Graupner, S. Tasch, G. Leising, K. Müllen, U. Scherf, *Appl. Phys. Lett.* **1997**, *71*, 2566. doi:10.1063/1.119332
- [7] X. Zhang, A. S. Shetty, S. A. Jenekhe, *Macromolecules* 1999, 32, 7422. doi:10.1021/MA990960+
- [8] X. Zhang, S. A. Jenekhe, *Macromolecules* 2000, 33, 2069. doi:10.1021/MA991913K
- [9] B. Hu, F. E. Karasz, J. Appl. Phys. 2003, 93, 1995. doi:10.1063/ 1.1536018
- [10] U. Mitschke, P. Bäuerle, J. Mater. Chem. 2000, 10, 1471. doi:10.1039/A908713C
- [11] D. R. Baigent, N. C. Greenham, J. Grüner, R. N. Marks, R. H. Friend, S. C. Moratti, A. B. Holmes, *Synth. Met.* **1994**, *67*, 3. doi:10.1016/ 0379-6779(94)90004-3
- [12] Z. H. Peng, Z. N. Bao, M. E. Galvin, Adv. Mater. 1998, 10, 680. doi:10.1002/(SICI)1521-4095(199806)10:9<680::AID-ADMA680>3.0.CO;2-H
- [13] A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* 2004, 16, 4556. doi:10.1021/CM049473L
- [14] A. P. Kulkarni, Y. Zhu, S. A. Jenekhe, *Macromolecules* 2005, *38*, 1553. doi:10.1021/MA048118D
- [15] G. Hughes, M. R. Bryce, J. Mater. Chem. 2005, 15, 94. doi:10.1039/B413249C
- [16] E.-M. Chang, F. F. Wong, T.-H. Chen, K.-C. Chiang, M.-Y. Yeh, *Heterocycles* 2006, 68, 1007. doi:10.3987/COM-06-10714
- [17] X. C. Li, F. Cacialli, M. Giles, J. Gruner, R. H. Friend, A. B. Homes, S. C. Moratti, T. M. Yong, *Adv. Mater.* **1995**, *7*, 898. doi:10.1002/ ADMA.19950071104
- [18] M. Ueda, M. Oda, Polym. J. 1989, 21, 193. doi:10.1295/ POLYMJ.21.193
- [19] C. Kummerloewe, H. W. Kammer, M. Malincomico, E. Martuscell, *Polymer* 1991, 32, 2505. doi:10.1016/0032-3861(91)90328-G
- [20] N. Tamoto, C. Adachi, K. Nagai, Chem. Mater. 1997, 9, 1077. doi:10.1021/CM960391+
- [21] Z. Peng, J. Zhang, Chem. Mater. 1999, 11, 1138. doi:10.1021/ CM981087E

- [22] S.-H. Hsiao, C.-H. Yu, J. Polym. Sci., Part A: Polym. Chem. 1998, 36, 1847. doi:10.1002/(SICI)1099-0518(199808)36:11<1847::AID-POLA18>3.0.CO;2-E
- [23] Y. Jin, J. Y. Kim, S. H. Park, J. Kim, S. Lee, K. Lee, H. Suh, *Polymer* 2005, 46, 12158. doi:10.1016/J.POLYMER.2005.10.080
- [24] J. A. Mikroyannidis, V. P. Barberis, L. Ding, F. E. Karasz, J. Polym. Sci., PartA: Polym. Chem. 2004, 42, 3212. doi:10.1002/POLA.20135
- [25] C. Wang, G.-Y. Jung, Y. Hua, C. Pearson, M. R. Bryce, M. C. Petty, A. S. Batsanov, A. R. Goeta, J. A. K. Howard, *Chem. Mater.* 2001, 13, 1167. doi:10.1021/CM0010250
- [26] M.-Y. Yeh, H.-J. Tien, L.-Y. Huang, M.-H. Chen, J. Chin. Chem. Soc. 1983, 30, 29.
- [27] H. Mayer, F. Staffen, Monatsh. Chem. 1913, 34, 525.
- [28] G. Li, X. Wang, F. Wang, *Tetrahedron Lett.* 2005, 46, 8971. doi:10.1016/J.TETLET.2005.10.113
- [29] D. R. McKean, G. Parrinello, A. F. Renaldo, J. K. Stille, J. Org. Chem. 1987, 52, 422. doi:10.1021/JO00379A020
- [30] B. Xu, Y. Pan, J. Zhang, Z. Peng, Synth. Met. 2000, 114, 337. doi:10.1016/S0379-6779(00)00271-X
- [31] A. Hilberer, H.-J. Brouwer, B.-J. Van der Scheer, J. Wildeman, G. Hardziioannou, *Macromolecules* 1995, 28, 4525. doi:10.1021/ MA00117A022
- [32] (a) H. Fang, S. Wang, S. Xiao, Y. Li, Y. Liu, L. Fan, Z. Shi, C. Du, D. Zhu, *Synth. Met.* 2002, *128*, 253. doi:10.1016/S0379-6779(01)00648-8
 (b) J. A. Mikroyannidis, I. K. Spiliopoulos, T. S. Kasimis, A. P. Kulkarni, S. A. Jenekhe, *J. Polym. Sci., Part A: Polym. Chem.* 2004, *42*, 2112. doi:10.1002/POLA.20049
- [33] Z. Wang, X. Yang, X. Chen, Z. Xu, X. Xu, *Thin Solid Films* 2000, 363, 94. doi:10.1016/S0040-6090(99)01011-1
- [34] M. Thelakkat, H.-W. Schmidt, Adv. Mater. 1998, 10, 219. doi:10.1002/(SICI)1521-4095(199802)10:3<219::AID-ADMA219> 3.0.CO;2-6