ORGANIC LETTERS

2003
Vol. 5, No. 6
839–842

Diphenylamino Group as an Effective Handle to Conjugated Donor–Acceptor Polymers through Electropolymerization

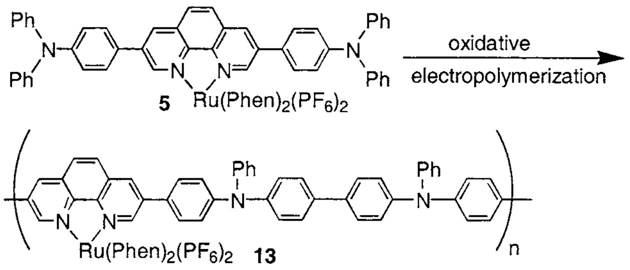
Man-kit Leung,* Meng-Yen Chou, Yuhlong Oliver Su,*,† Chang Ling Chiang, Hung-Lin Chen, Chin Fu Yang, Chih-Chiang Yang, Chang-Chih Lin, and Hung-Ting Chen

Department of Chemistry, National Taiwan University, Taipei,
Taiwan 106, Republic of China, Department of Chemistry,
National Chi Nan University, Nantou, Taiwan 545, Republic of China

mkleung@ms.cc.ntu.edu.tw

Received December 16, 2002

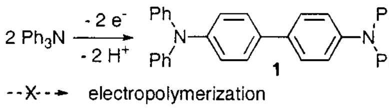
ABSTRACT



The diphenylamino group is an effective handle for electropolymerization to give electron donor–acceptor conjugated polymers. In addition, interesting electrochromic and photoresponsive behavior of 13 has been investigated.

Because of their unusual optical, electrical, and electronic properties, conjugated polymers containing electron donor–acceptor pairs have become an important area of study.[1] The family of triarylamines attracts us because of their excellent hole-transporting properties. However, triphenylamine (TPA), the smallest member in this family, is electrochemically active toward oxidation[2] and is rarely used for device applications. Previous study revealed that although TPA is known to dimerize through electrochemical oxidation to give *N*,*N*,*N*′,*N*′-tetraphenyl-4,4′-diaminobiphenyl (TPB **1**), **1** does not effectively couple to give polymers (Scheme 1). Therefore, unlike thiophene[3] or pyrrole,[4] the diphenylamino group has seldom been used as a handle for electropolymerization.

Scheme 1



Cyclic voltammetric analysis (CV) of **1** shows two reversible oxidative waves at 305 and 550 mV with respect to ferrocene (Fc) internal standard. The electrochemical inertness of **1**

[†] National Chi Nan University.

[1] (a) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15. (b) Ng, S. C.; Lu, H.-F.; Chan, H. S. O.; Fujii, A.; Laga, T.; Yoshino, K. *Adv. Mater.* **2000**, *12*, 1122. (c) Bao, Z.; Peng, Z.; Galvin, M. E.; Chandross, E. A. *Chem. Mater.* **1998**, *10*, 1201. (d) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376. (e) Wu, A. P.; Jikei, M.; Kakimoto, M.; Imai, Y.; Ukishima, S.; Takahashi, Y. *Chem. Lett.* **1994**, 2319.

[2] Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498.

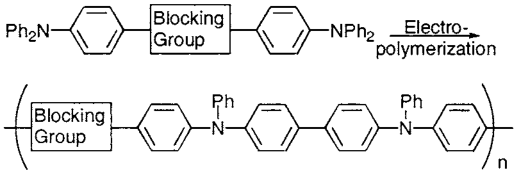
[3] (a) Hay, C.; Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1812. (b) Buey, J.; Swager, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 608. (c) Hjelm, J.; Constable, E. C.; Figgemeier, E.; Hagfeldt, A.; Handel, R.; Housecroft, C. E.; Mukhtar, E.; Schofield, E. *Chem. Commun.* **2002**, *3*, 284. (d) Lin, S.-C.; Chen, J.-A.; Liu, M.-H.; Su, Y. O.; Leung, M.-k *J. Org. Chem.* **1998**, *63*, 5059.

[4] (a) Komaba, S.; Fujihana, K.; Osaka, T.; Aiki, S.; Nakamura, S. *J. Electrochem. Soc.* **1998**, *145*, 1126. (b) Wu, Q.; Storrier, G. D.; Pariente, F.; Wang, Y.; Shapleigh, J. P.; Abruña, H. D. *Anal. Chem.* **1997**, *69*, 4856. (c) Sotzing, G. A.; Reynolds, J. R.; Katritzky, A. R.; Soloducho, J.; Belyakov, S.; Musgrave, R. *Macromolecules* **1996**, *29*, 1679. (d) Carvalho de Medeiros, M. A.; Cosnier, S.; Deronzier, A.; Moutet, J.-C. *Inorg. Chem.* **1996**, *35*, 2659.

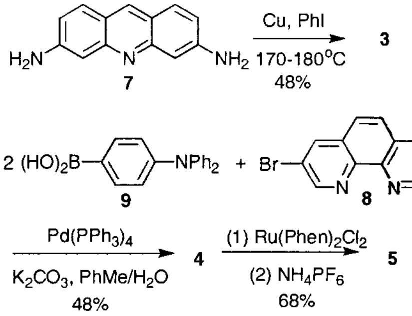
10.1021/ol027474i CCC: $25.00

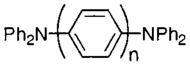
and its relatively low first oxidation potential are attributed to resonance delocalization of the radical-cation between two nitrogen atoms. On the basis of this assumption, we foresee that introduction of a blocking group between the amino units would prevent the radical-cations from delocalization, resuming their reactivity toward electropolymerization.[5] To block the resonance interactions, we have examined two different tactics, including (1) extending the number of phenylene units[6] and (2) introduction of electron-deficient components. Particularly if the second tactic is successful, electron-donating TBP units will be directly formed through electropolymerization, providing alternativng conjugated donor−acceptor polymers (Scheme 2).To evaluate the feasibility of this approach, we selected five monomers **2**−**6** to study. Compound **2**[7] shows a two-electron reversible oxidation at 500 mV. Although monomer **2** contains more phenylene units in comparison to **1**, no sign for polymeric film growth was observed according to the cyclic voltammetric analysis, indicating that simple extension of the conjugation length does not effectively prohibit the radical-cation from delocalization. The syntheses of acridine, phenanthroline, and oxadiazole containing monomers **3**−**6** are shown in Schemes 3 and 4. Their physical properties are summarized in Table 1. In contrast to monomer **2**, the heterocyclic aromatic units in **3**−**6** are known to have a low-lying HOMO[8] and could be considered as hole-blocking units. Tetraphenylation of **7**, using Ullman conditions,[9] led to **3** in 48% yield. On the other hand, Suzuki coupling[10] of 3,8-dibromophenanthroline **8**[11] with boronic acid **9**[12] gave **4** in moderated yield. On treatment of **4** with *cis*-(Phen)$_2$RuCl$_2$, a ruthenium chloride complex was formed.[13] To prevent the interference of Cl$^-$ from oxidative electropolymerization, the chloride ions were removed by ion exchange with PF$_6^-$ to form **5**.

Scheme 2

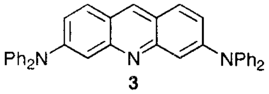


Scheme 3

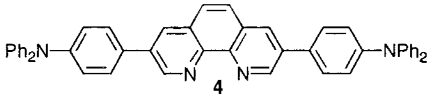




2 n = 4

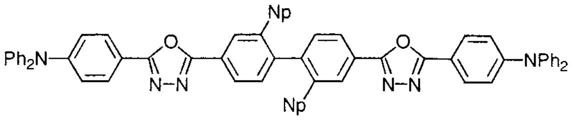


3



4

5 Ru(Phen)$_2$(PF$_6$)$_2$ complex



6 Np: 1-Naphthyl

Suzuki coupling of dimethyl 2,2′-diiodobiphenyl-4,4′-dicarboxylate **10**[14] with 1-naphthaleneboronic acid[15,16] gave **11** in high yield.[17] Treatment of **11** with hydrazine and 4-bromobenzoyl chloride, followed by a dehydrative cyclization with POCl$_3$ led to oxadiazole **12** in a 59% overall yield.[18] Finally, palladium-catalyzed amination of **12**, using Buchwald−Hartwig conditions,[19] afforded **6** as a glassy material. Although the restricted rotation of the 1-naphthyl groups led to coalecsed aromatic signals that are difficult to assign in their ^{1}H NMR spectra, all the structural assignments are consistent with the results of the high-resolution mass spectra as well as elemental analyses. The oxidative electrochemical behavior of **3**−**6** was examined by CV on Pt electrodes in CH$_2$Cl$_2$ with (Bu)$_4$NPF$_6$ (0.1 M) as the supporting electrolyte and Ag/AgCl (sat’d) as the reference electrode (Table 1). Compounds **3**−**5** show a characteristic oxidation wave in the first CV scan at around 500−550 mV that corresponds to the arylamine oxidation. Perhaps due to the electron-withdrawing properties of the oxadiazole unit, **6** shows a higher oxidation potential at 630 mV. The presence

---

(5) (a) Lambert, C. Private communication. (b) Paterson, M. A.; Brown, B.; Cherryman, J.; Puschmann, H.; Howard, J. A. K.; Low, P. J. Symposium Proceeding of The fifth international symposium on functional π-electron system, 2001, 365 (poster 299). Germany.

(6) Lambert, C.; Nöll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434.

(7) Available from Syntec-Synthon Co. Germany.

(8) (a) Wang, C.; Jung, G.-Y.; Batsanov, A. S.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **2002**, *12*, 173. (b) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077.

(9) Yamamoto, T.; Kurata, Y. *Can. J. Chem.* **1983**, *61*, 86.

(10) For review, see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Mathews, C. J.; Smith, P. J.; Welton, T. *Chem. Commun.* **2000**, *14*, 1249.

(11) Joshi, H. S.; Jamshidi, R.; Tor, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 2725.

(12) Wong, K.-T.; Chien, Y.-Y.; Liao, Y.-L.; Lin, C.-C.; Chou, M.-Y.; Leung, M.-k. *J. Org. Chem.* **2002**, *67*, 1041.

(13) Burdinski, D.; Bothe, E.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 105.

(14) Kwong, C.-Y.; Chan, T.-L.; Chow, H.-F.; Lin, S.-C.; Leung, M.-k. *J. Chin. Chem. Soc.* **1997**, *44*, 211

(15) Qian, Y.; Marugan, J. J.; Fossum, R. D.; Vogt, A.; Sebti, S. M.; Hamilton, A. D. *Bioorg. Med. Chem.* **1999**, *7*, 3011.

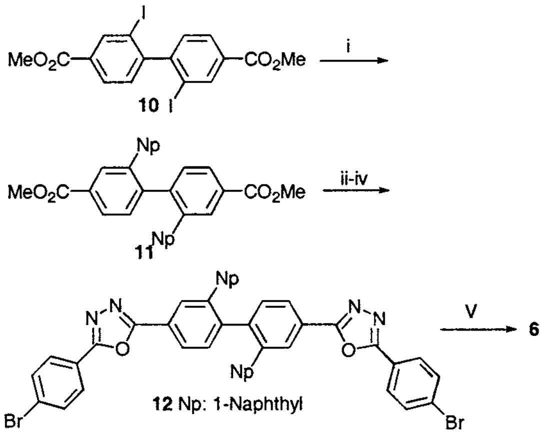
(16) Qian, Y.; Marugan, J. J.; Fossum, R. D.; Vogt, A.; Sebti, S. M.; Hamilton, A. D. *Bioorg. Med. Chem.* **1999**, *7*, 3011.

(17) Yang, C. F.; Chen, H.-D.; Yang, K. H.; Leung, M.-k.; Wu, C.-C.; Yang, C. C.; Wang, C. C.; Fann, W. S. *Mater. Sci. Eng.* **2001**, *B85* (2−3), 236.

(18) Popova, N. A.; Yushko, E. G.; Krasovitskii, B. M.; Minkin, V. I.; Lyubarskaya, A. E.; Gol’dberg, M. L. *Chem. Heterocycl. Compd.* **1983**, 22.

(19) (a) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (b) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805.

Scheme 4 [a]



[a] Reagents: (i) $NpB(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3 PhH/H_2O, 80%; (ii) $N_2H_4 \cdot H_2O$, 95%; (iii) 4-BrC_6H_4COCl, 94%; (iv) $POCl_3$, 66%; (v) Ph_2NH, Pd_2dba_3, $P(t\text{-}Bu)_3$, ^{t}BuONa, PhMe, 84%.

of the second reversible oxidation at 970 mV for **5** is attributed to the oxidation of the Ru(II) to Ru(III).[21]

Athough monomers **3**−**6** have an oxidation potential similar to that of **2**, their electrochemical behavior is extremely different. Repeating the CV cycles gives new oxidation waves around 350−450 and 530−580 mV (Table 2). The oxidation currents increase when the number of the cycles increases, indicating formation of a polymeric film on the electrode.

Table 1. Optical and Electrochemical Properties of **1**−**6**

	UV (nm)^{a,c}		$E_{1/2}$ (mV)^{b,c}	
TBP 1	311, 351	305	550	
2	312, 358		500	
3	292, 335, 451		510	880
4	292, 392		560	
5	288, 459		570	970
6	293, 373		630	

[a] In $CHCl_3$. [b] Estimated $E_{1/2}$ vs Fc^+/Fc. [c] For the molar absorptivites and peak-to-peak values of the redox couples, see the Supporting Information.

Table 2. Optical and Electrochemical Properties of the Polymeric Films from Monomers **3**−**6**

		$E_{1/2}$ (mV)^b	
	UV (nm)^a	reduction^c	oxidation^d
3	316, 548	−2270	670, 840
4	366, 400	−2430	370, 520
5	338, 452	−1710, −1930 −2320, −2570	390, 510, 900
6	384	−2390, −2570	470, 580

[a] Film on ITO. [b] $E_{1/2}$ vs Fc^+/Fc.[20] [c] In THF. [d] In CH_2Cl_2.

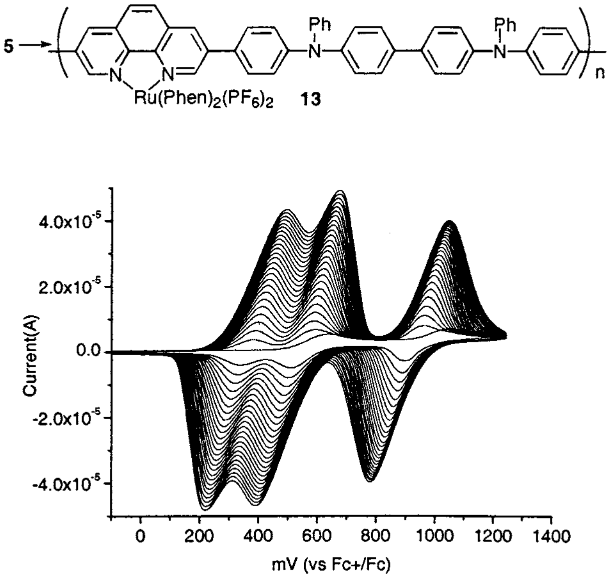


Figure 1. CV diagram for electropolymerization of **5** (0.6 mM) to **13** in CH_2Cl_2.

An example shown in Figure 1 is the CV diagram for electropolymerization of **5** to give **13**. Comparing the positions of the $E_{1/2}$ against that of **1** suggests formation of the TBP linkage in polymerization. It is noteworthy to mention that reduction waves between 1700 and 2600 mV relative to ferrocene could also be observed for each of the polymers, indicating their electron donating−accepting amphoteric properties (Figure 2). Perhaps due to their good positive-charge transporting properties, polymeric film growth is particularly effective.

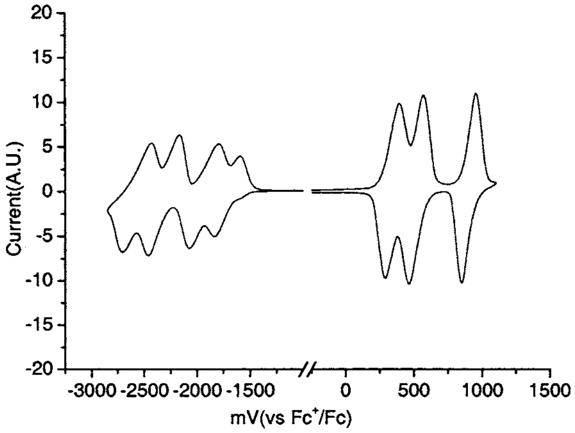


Figure 2. CV diagram for the thin film of **13** on a Pt electrode with $(Bu)_4NPF_6$ (0.1 M) as the supporting electrolyte in THF for reduction and CH_2Cl_2 for oxidation.

---

(20) The $E_{1/2}$ values of Fc are 615 mV in THF and 470 mV in CH_2Cl_2.

(21) Yang, X.-J.; Janiak, C.; Heinze, J.; Drepper, F.; Mayer, P.; Piotrowski, H.; Klüfers, P. *Inorg. Chim. Acta* **2001**, *318*, 103.

Electrochromism[22] of **13** was examined by direct electrochemical deposition of the polymer onto an ITO glass and its absorption was monitored by a UV−Vis−NIR spectrometer (Figure 3). In the neutral state, the orange polymer **13** shows an intense absorption at 452 nm. On oxidation, the film gives a new absorption signal in the NIR region, ranging from 1000 to 2000 nm. Further oxidation of the film leads to absorption at around 800 nm, and the film turns a deep blue-green color.

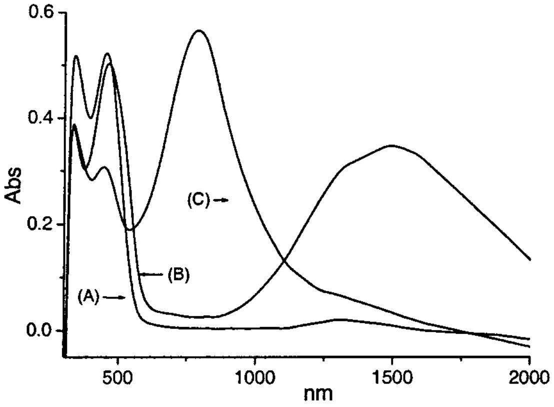


Figure 3. Electrochromic behavior of **13** at an electrical potential of (A) 0, (B) 0.9, and (C) 1.3 V vs Ag/AgCl (sat'd) as the reference in CH_2Cl_2, and with 0.1 M of $(Bu)_4NClO_4$ as the supporting electrolyte.

The stability of the polymer film in air was found to be extremely good. After being dried up and left on the benchtop for one week, the electrochromic properties of the sample could simply be restored by reinsertion back to a supporting electrolyte.

The photoresponsive behavior of **13** has also been studied preliminarily by our research team. Derivatives of ruthenium phenanthroline complexes are known to be effective dyes for solar voltaic application.[23] In our experiments, polymer **13** was deposited onto a TiO_2-coated ITO glass, followed by vacuum vapor deposition of a layer of aluminum as the electrode. As shown in Figure 4, photoconductivity of the device could be observed under 1 V of bias. Using either a UV lamp for TLC analysis or a flashlight could trigger the photocurrent. Without the polymer layer, no electrical response could be observed under irradiation, indicating that the photoresponsive behavior is arising from the polymeric dye layer.

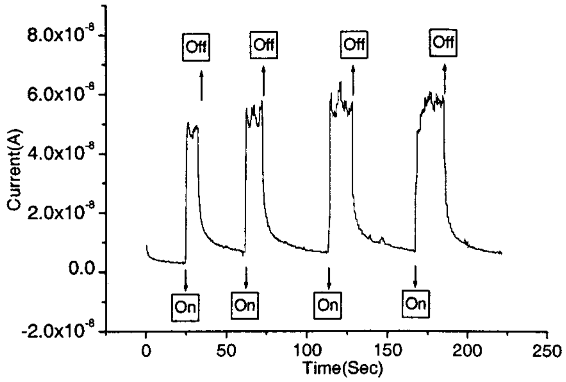


Figure 4. Photocurrent from a device of ITO/TiO_2/**13**/Al under the bias of 1 V with ITO as the anode and Al as the cathode.

In summary, we provide a convenient and effective method to access conjugated polymers containing electron donor−acceptor pairs. We also clearly demonstrate that this electrochemical approach could be applied to a wide variety of applications.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (NSC 91-2113-M-002-024).

Supporting Information Available: Procedures for the synthesis and characterization data, general procedures for electropolymerization and for spectroelectrochemistry of **3−6,** fabrication and measurement of the photodiode and electrochromic devices from **5**, oxidative and reductive CV diagrams for the polymers of **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL027474I

---

[22] Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. In *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, Germany, 1995.

[23] Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Gratzel, M. *Nature* **1998**, *395*, 585.