Date: 19-09-12 17:50:49

Pages: 5

Synthesis and Physicochemical Properties of Strong Electron Acceptor 14,14,15,15-Tetracyano-6,13-pentacenequinodimethane (TCPQ) Diimide

Jie Li,^[a] Yu Xiong,^[a] Oinghe Wu,^[a] Shitao Wang,^[a] Xike Gao,^[a] and Hongxiang Li*^[a]

Keywords: Cycloaddition / Conjugation / Diimide / Electrochemistry / UV/Vis spectroscopy

14,14,15,15-Tetracyano-6,13-pentacenequinodimethane (TCPQ) diimide, a new tetracyanoquinodimethane analogue with extended conjugation and imide substituents, was synthesized by double Diels-Alder reactions and a Knoevenagel condensation reaction. Experimental results showed that TCPQ diimide has a low LUMO energy level (-4.03 eV) and good solubility in organic solvents.

Introduction

Organic semiconductors with electron-withdrawing properties (organic electron acceptors) have attracted great attention because of their wide applications in organic electronic devices such as organic thin-film transistors (OTFTs),^[1] organic photovoltaics (OPVs),^[2] and organic light-emitting diodes (OLEDs).^[3] Though great effort has been devoted to the field of organic electron acceptors, the development of organic electron acceptors still largely lags behind that of organic electron donors (organic semiconductors with electron donating properties). Moreover, there is a great need to design and synthesize new types of organic electron acceptors, especially those with lowest unoccupied molecular orbital (LUMO) energy levels lower than -4.0 eV.^[4]

Tetracyanoquinodimethane (TCNQ, Scheme 1) is a wellknown organic electron acceptor with a very low LUMO energy level (-4.6 eV). It has been used in charge-transfer (CT) complexes,^[5] electrical and optical memory devices,^[6] switching devices,^[6a,7] and sensors.^[8] However, the short conjugation length and low solubility of TCNQ hinders its further applications in organic electronics. Hence, TCNQ analogues such as tetracyanoanthraquinodimethane (TCAQ)^[9] and 15,15,16,16-tetracyano-6,13-pentacenequinodimethane (TCPQ^[10], Scheme 1) were synthesized with the aim to increase the conjugation length. Very recently, Chi et al.^[11] prepared a seven-ring fused TCNQ analogue 19,19,20,20-tetracyano-7,16-tetrakis(5'-dodecylthieno)-[a,c,p,r]1). Unfortunately, the LUMO energy level of TCNQ

Organic Chemistry, Chinese Academy of Sciences,

Shanghai, 200032, China Fax: +86-21-54925024

E-mail: lhx@sioc.ac.cn

Homepage: http://sourcedb.sioc.cas.cn/cn/expert/br/200906/ t20090621 1750754.html

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201065.

analogues increases dramatically with the increase in conjugation length, which eliminates the unique properties of TCNQ. Till now, only a few examples of TCNQ analogues with LUMO energy levels lower than -4.0 eV have been explored.



Scheme 1. The chemical structures of TCNQ, TCAQ, TCPQ, TCTTHQ, TPAFO, and PDPTP.

Arylene diimides generally have low LUMO energy levels due to the electron-withdrawing effects of the diimide groups. The most representative compounds of arylene diimides are naphthalene diimides (NDI)^[12] and perylene diimides (PDI),^[13] which have a LUMO energy level lying at about -3.80 and -3.85 eV, respectively. In addition, the solubility of the arylene diimides can be easily improved by changing the substituents on the N atoms. Considering the

[[]a] Laboratory of Material Sciences, Shanghai Institute of

SHORT COMMUNICATION

merits of diimide substituents, herein TCPQ diimide (1), a new TCNQ analogue with extended conjugation and diimide substituents, was synthesized. The physicochemical properties of 1 were also investigated.

Results and Discussion

The synthetic route to **1** is outlined in Scheme 2. Diimide-substituted pentacenedione compound **7** is the key intermediate in this pathway. The 4,8,12,16-substituted derivative of compound **7**, 4,8,12,16-tetraphenyl-2,10-dimethylpentaceno[2,3-c:9,10-c']dipyrrole-1,3,6,9,11,14(2H,10H)hexone (PDPTP,^[14] Scheme 1), was synthesized by treating 1,3,7,9-tetrakisphenylanthra[2,3-c:6,7-c]difuran-5,11-dione (TPAFO, Scheme 1) with *N*-alkylmaleimide followed by aromatization in the presence of concentrated sulfuric acid. In this procedure, the synthesis of TPAFO requires nine tedious synthesis steps from commercially available fumaryl chloride. In this paper, a new synthetic route to synthesize compound **7** was developed.

Starting from maleic anhydride and 3,4-dimethylbutadiene, N-(2-ethylhexyl)-4,5-dimethyl-*cis*-4-tetrahydrophthalimide (**4**) was synthesized by two procedures. In the first method, maleic anhydride was treated with 2-ethylhexylamine, followed by Ac₂O-mediated dehydration in the presence of AcONa to give N-2-ethylhexylmaleimide (**2**) in 50% yield. Then, Diels–Alder cycloaddition between **2** and 3-dimethylbutadiene afforded **4** in nearly quantitative yield. The low yield of the first step limited the applications of this method.^[15] In the second procedure, 2,3-dimethylbutadiene was first treated with maleic anhydride to afford cycloaddition product 3, and 3 was then treated with 2-ethylhexylamine to give 4. The total yield of the second procedure was $\approx 73\%$. *N*-(2-Ethylhexyl)-4,5-dimethylphthalic imide (5) was synthesized in 78% yield by sulfur-mediated oxidation of 4. Imide 5 was brominated with NBS in the presence of benzoyl peroxide (BPO) to give 6. Key intermediate 7 was prepared by treating 6 with 1,4-benzoquinone in dry DMF.

A new synthetic method to further simplify the synthesis of 7 was also tried (Scheme 3). In this procedure, pyromellitic dianhydride was firstly treated with 2-ethylhexylamine (1 equiv.) to afford monoimide compound 8, which was then reduced to afford 9 on the basis of the different reactivities of the imide and anhydride functionalities. Oxidization of 9 afforded dialdehyde 10, which was further treated with cyclohexane-1,4-dione to give 7. However, the reduction potentials of the imide and anhydride functionalities in 8 are close; thus, a very low yield was obtained, which hindered the application of this method.

Target product **1** was synthesized by Knoevenagel condensation of **7** with the Lehnert reagent^[16] (TiCl₄, malononitrile, pyridine) and obtained as a yellow solid. Compound **1** had good solubility in organic solvents such as CH₂Cl₂, CHCl₃, and THF and was characterized by NMR spectroscopy and mass spectrometry. Figure 1 illustrates the UV/Vis spectrum of compound **1** in chloroform solution. Three peaks are observed in the absorption spectra, which are located at 416, 330, and 295 nm. The maximum absorption wavelength of **1** was the same as that of TCPQ^[10] (415 nm in chloroform) and about 69 nm redshifted compared to that of TCAQ^[17] (347 nm in dichloromethane),



Scheme 2. Synthetic route to compound 1.

Date: 19

Date: 19-09-12 17:50:49

Pages: 5

Synthesis and Physicochemical Properties of a Strong Electron Acceptor



Scheme 3. Another possible route to key intermediate 7.

which can be ascribed to the enlarged conjugation length of **1**. The HOMO–LUMO energy band gap estimated from the initial absorption was 2.79 eV.



Figure 1. UV/Vis spectrum of 1 in chloroform solution $(1 \times 10^{-5} \text{ M})$.

The electrochemical properties of compound 1 were investigated by cyclic voltammetry (CV). To compare with other TCNQ analogues, CV was carried out in a CH₃CN solution by using SCE as the reference electrode and ferrocene as the internal standard reference. The redox potential of 1 is listed in Table 1 together with those of TCNQ, TCAQ, TCPQ, and TCTTHQ. Compound 1 exhibited two reversible reduction waves (Figure 2). The first half-wave reduction potential was -0.38 V, which is lower than that of TCPQ and close to that of TCAQ. In view of its good solubility and a LUMO energy level that is similar to that of TCAQ, compound 1 displays great potential applications in solution as possible organic field emission and switch devices.^[18] The LUMO energy level of compound 1 calculated from CV was -4.03 eV, which is much lower than that of TCTTHQ (LUMO, -3.67 eV).[11] Though the conjugation length of 1 is shorter than that of TCTTHQ, its low LUMO energy level and good solubility in organic solvents suggest that compound 1 would be a good candidate as solution-processed, ambient-stable n-channel organic semiconductors.



Table 1. Cyclic voltammetry data for 1, TCNQ, TCAQ, and TCPQ.

Compound	Solvent	$E_{1/2}^{(1)}(\mathbf{V})$	$E_{1/2}^{(2)}(\mathbf{V})$	LUMO ^[a] [eV]
TCNQ ^[19]	CH ₃ CN	0.08	-0.48	
TCAQ ^[20]	CH ₃ CN	-0.285		
TCAQ ^[9a]	CH ₃ CN	-0.46	-0.65	
TCPQ ^[10]	CH ₃ CN	-0.57	-0.91	
TCTTHQ ^[11]	CH_2Cl_2	-0.82		-3.67
1	CH ₃ CN	-0.38	-1.10	-4.03

[a] The LUMO was calculated based on $E_{\text{LUMO}} = -(4.8 - F_c/F_c^+ + E^{1/2})$.



Figure 2. Cyclic voltammetry of 1 in CH_3CN solution: Bu_4NF as electrolyte, Pt as working electrode, Pt wire as counter electrode, and SCE as reference electrode. Ferrocene was used as internal standard.

Conclusions

In summary, a new type of TCNQ analogue, compound 1, with extended conjugation and diimide substituents was successfully synthesized. In the preparation of 1, a new method that can simplify the synthesis of the key intermediate, diimide-substituted pentacenedione 7, was developed. Compound 1 has a low LUMO energy level (-4.03 eV) and displays good solubility in organic solvents, suggesting the potential use of 1 in organic electronics. The application of compound 1 in devices such as thin-film transistors is underway in our laboratory.

Supporting Information (see footnote on the first page of this article): Experimental details and copies of the ¹H NMR, ¹³C NMR, and mass spectra of all key intermediates and final products.

Acknowledgments

This work was supported by the National Natural Sciences Foundation of China (21190031) and the National Basic Research Program of China (2011CB808405)

- a) J. Zaumseil, H. Sirringhaus, *Chem. Rev.* 2007, 107, 1296; b)
 Y. G. Wen, Y. Q. Liu, *Adv. Mater.* 2010, 22, 1331.
- [2] a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Science 1995, 270, 1789; b) P. Peumans, V. Bulovic, S. R. Forrest, Appl. Phys. Lett. 2000, 76, 2650; c) J. D. MacKenzie, R. H. Friend, E. Moons, A. Fechtenkotter, L. Schmidt-Mende, K. Mullen, Science 2001, 293, 1119; d) C. Uhrich, R. Schueppel, A. Petrich, M. Pfeiffer, K. Leo, E. Brier, P. Kilickiran, P. Baeuerle, Adv. Funct. Mater. 2007, 17, 2991; e) C. L. Chochos, S. P. Economopoulos, V. Deimede, V. G. Gregoriou, M. T. Lloyd, G. G. Malliaras, J. K. Kallitsis, J. Phys. Chem. C 2007, 111, 10732; f) C. H. Hsieh, Y. J. Cheng, P. J. Li, C. H. Chen, M.

SHORT COMMUNICATION

Dubosc, R. M. Liang, C. S. Hsu, J. Am. Chem. Soc. 2010, 132, 4887.

- [3] For example, see: a) J. Luo, X. Li, J. Peng, W. Yang, Y. Cao, *Adv. Mater.* 2007, *19*, 1113; b) J. Liu, Y. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Mater.* 2005, *17*, 2974.
- [4] Organic electron acceptors with LUMO energy levels lower than -4.0 eV play important roles in organic electronics. See, for example: a) B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski, Angew. Chem. 2004, 116, 6523; Angew. Chem. Int. Ed. 2004, 43, 6363; b) Z. Wang, C. Kim, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2007, 129, 13362; c) B. A. Jones, A. Facchetti, M. R. Wasielewski, T. J. Marks, J. Am. Chem. Soc. 2007, 129, 13362; c) B. A. Jones, A. Facchetti, M. R. Wasielewski, T. J. Marks, J. Am. Chem. Soc. 2007, 129, 15259; d) J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao, C. L. Wilkins, J. Org. Chem. 1995, 60, 532; e) G. Dennler, M. C. Scharber, C. J. Brabec, Adv. Mater. 2009, 21, 1323 and references cited therein.
- [5] a) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, W. E. Mochel, *J. Am. Chem. Soc.* **1962**, *84*, 3374; b) J. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948; c) M. R. Bryce, L. C. Murphy, *Nature* **1984**, *309*, 119; d) A. F. Garito, A. J. Heeger, *Acc. Chem. Res.* **1974**, *7*, 232.
- [6] a) R. Potember, T. Poehler, D. Cowan, *Appl. Phys. Lett.* 1979, 34, 405; b) C. Sato, S. Wakamatsu, K. Tadokoro, K. Ishii, *J. Appl. Phys.* 1990, 68, 6535; c) A. Hefczyc, L. Beckmann, E. Becker, H. H. Johannes, W. Kowalsky, *Phys. Status Solidi A* 2008, 205, 647.
- [7] a) Z.-Z. Gu, H. Wu, Y. Wei, J. Liu, J. Phys. Chem. 1993, 97, 2543; b) T. Oyamada, H. Tanaka, K. Matsushige, H. Sasabe, C. Adachi, Appl. Phys. Lett. 2003, 83, 1252.

- [8] a) J. Kulys, E. J. DaCosta, *Biosens. Bioelectron.* 1991, *6*, 109;
 b) T. J. Wooster, A. M. Bond, M. J. Honeychurch, *Anal. Chem.* 2003, *75*, 586.
- [9] a) S. Yamaguchi, G. Tatemitsu, Y. Sakata, S. Misumi, *Chem. Lett.* **1983**, 1229; b) B. S. Ong, B. Keoshkerian, *J. Org. Chem.* **1984**, 49, 5002.
- [10] a) N. Martin, M. Hanack, J. Chem. Soc., Chem. Commun. 1988, 1522; b) N. Martin, R. Behnisch, M. Hanack, J. Org. Chem. 1989, 54, 2563.
- [11] Q. Ye, J. Chang, K. W. Huang, G. Dai, J. Zhang, Z. K. Chen, J. Wu, C. Chi, Org. Lett. 2012, 14, 2786.
- [12] H. E. Katz, J. Johnson, A. J. Lovinger, W. Li, J. Am. Chem. Soc. 2000, 122, 7787.
- [13] P. R. L. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, *Appl. Phys. Lett.* 2002, 80, 2517.
- [14] a) T. Chiba, P. W. Kenny, L. L. Miller, J. Org. Chem. 1987, 52, 4327; b) P. W. Kenny, T. H. Jozefiak, L. L. Miller, J. Org. Chem. 1988, 53, 5007.
- [15] a) L. Coleman, J. Bork, H. Dunn, J. Org. Chem. 1959, 24, 135;
 b) B. Pal, P. K. Pradhan, P. Jaisankar, V. S. Giri, Synthesis 2003, 1549.
- [16] a) W. Lehnert, *Tetrahedron Lett.* 1970, 11, 4723; b) W. Lehnert, *Synthesis* 1974, 667.
- [17] F. Bureš, W. B. Schweizer, C. Boudon, J. Gisselbrecht, M. Gross, F. Diederich, *Eur. J. Org. Chem.* 2008, 994.
- [18] S. Cui, Y. Li, Y. Guo, H. Liu, Y. Song, J. Xu, J. Lv, M. Zhu, D. Zhu, Adv. Mater. 2008, 20, 309.
- [19] A. Aumuller, S. Hunig, Liebigs Ann. Chem. 1984, 618.
- [20] A. M. Kine, D. O. Cowan, F. Gerson, R. Mockel, J. Am. Chem. Soc. 1985, 107, 556.

Received: August 7, 2012 Published Online: ■ Date: 19-09-12 17:50:49

Pages: 5

Synthesis and Physicochemical Properties of a Strong Electron Acceptor



Electron Acceptors

ᆗ

14,14,15,15-Tetracyano-6,13-pentacenequinodimethane (TCPQ) diimide, a new tetracyanoquinodimethane analogue with extended conjugation and imide substituents, was synthesized by double Diels-Alder reactions and a Knoevenagel condensation reaction. Experimental results showed that TCPQ diimide has a LUMO energy level (-4.03 eV) and good solubility in organic solvents.



LUMO: -4.03 eV



J. Li, Y. Xiong, Q. Wu, S. Wang, X. Gao, H. Li* 1-5

Synthesis and Physicochemical Properties of Strong Electron Acceptor 14,14,15,15-Tetracyano-6,13-pentacenequinodimethane (TCPQ) Diimide

Keywords: Cycloaddition / Conjugation / Diimide / Electrochemistry / UV/Vis spectroscopy