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通过电化学脱氢 N—N 偶联合成四取代肼化合物

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摘要 通过电氧化二级芳胺合成了一系列四取代肼化合物. 该电合成反应采用简单的装置如单室电解槽和恒电流电解, 且无需过渡金属催化剂和氧化试剂, 并可放大至克级规模.

关键词 有机电合成; 电氧化; 脱氢偶联; 四取代肼

Electrochemical Synthesis of Tetrasubstituted Hydrazines by Dehydrogenative N—N Bond Formation

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Abstract An electrochemical synthesis of tetrasubstituted hydrazines through dehydrogenative dimerization of secondary amines has been developed. The reactions are conducted in a simple undivided cell with constant current. The use of electricity to promote the reactions obviates the need for transition metal catalysts and oxidizing reagents, providing an efficient and sustainable access to tetrasubstituted hydrazines with diverse electronic properties.

Keywords organic electrosynthesis; anodic oxidation; dehydrogenative coupling; tetrasubstituted hydrazines

1 Introduction

Tetrasubstituted hydrazines have been found in natural products and materials (Scheme 1A).[1] We have recently discovered that 1,1,2,2-tetrakis(4-(*tert*-butyl)phenyl)-hydrazine is an efficient redox catalyst for electrosynthesis.[2] Tetrasubstituted hydrazines can be synthesized through transition metal-catalyzed oxidative coupling of secondary amines in the presence of a terminal oxidant such as oxygen or diaziridinone.[3] While these methods are attractive, the use of transition metal catalysts cause the concern of trace-metal contamination of the product.

Organic electrochemistry, which employs traceless electron as "reagents" to achieve redox reactions, has been attracting increasing interests among organic chemists.[4,5] In addition to its reagent-free feature, electrochemical methods can achieve transformations difficult for alternative methods that employ chemical oxidants. As an example, Baran and coworkers reported that the electrochemical oxidation outperformed chemical oxidants in promoting the N—N dimerization of carbazoles.[6] In this method, careful control of the electrode potential is essential for success. We have been interested in developing novel redox catalysts for organic electrosynthesis.[7] To further explore the potential of tetrasubstituted hydrazines as redox catalysts, we need an transition metal-free and scalable method to access these compounds. Herein we report the development of an electrochemical synthesis of tetrasubstituted hydrazines through dehydrogenative dimerization of secondary arylamines (Scheme 1B). The reactions are conveniently carried out under constant current conditions in an undivided cell.

2 Results and discussion

The oxidative dimerization of bis(4-(*tert*-butyl)phenyl)-amine (**1a**) was selected as a model reation to search for optimal electrolysis conditions (Table 1). Screening experiments revealed that an isolated yield of 89% of tetraarylhydrazine **2a** could be obtained when the reaction was carried out in a mixed solvent of tetrahydrofuran (THF)/MeOH (V∶V=3∶1) in the presence of 1 equiv. pyridine (Entry 1). Conveniently, the electrolysis was conducted using a constant current (j_{anode}=0.1 mA•cm^{-2})

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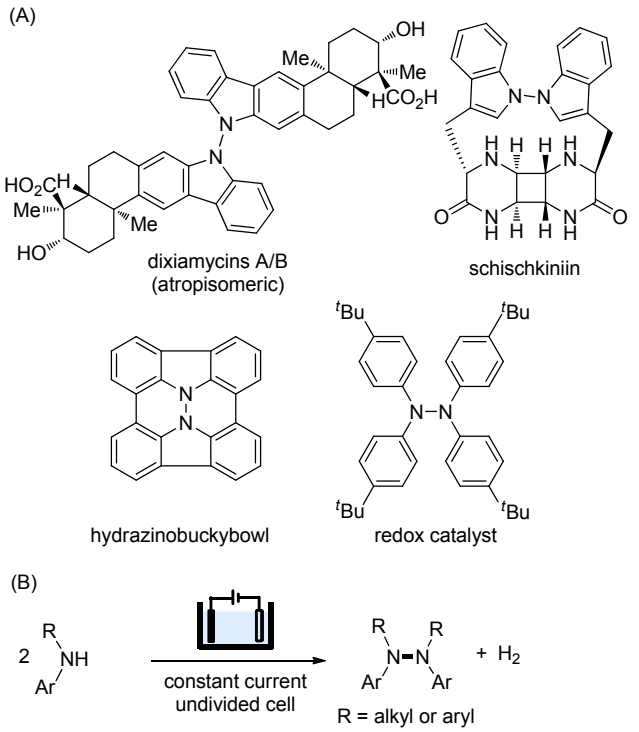
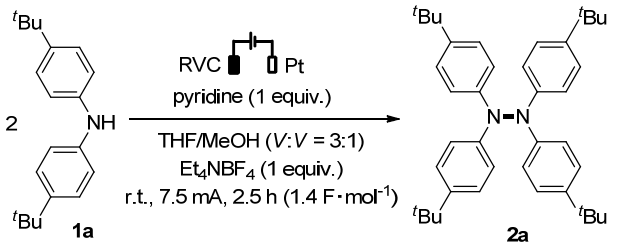


Scheme 1 (A) Selected compounds containing the tetrasubstituted hydrazine moiety, and (B) electrochemical dehydrogenative dimerization of secondary amines

Table 1 Optimization of reaction conditions[a]



Entry	Deviation from the standard condition	Yield[b]/%
1	None	96 (89)[c]
2	No base	64[c]
3	0.5 equiv. pyridine as base	91
4	1 equiv. KOAc as base	93
5	1 equiv. K_2CO_3 as base	94
6	1 equiv. $KHCO_3$ as base	95
7	THF/MeOH (V∶V=1∶3) as solvent	38
8	THF/MeOH (V∶V=1∶1) as solvent	93
9	Under air	93

[a] Reaction conditions: RVC anode, Pt plate cathode, undivided cell, **1a** (0.5 mmol), base (0.5 mmol), solvent (10 mL), Et_4NBF_4 (0.5 mmol), r.t.. [b] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yield.

in an undivided cell equipped with a reticulated vitreous carbon (RVC) anode and a platinum plate cathode. The basic additive was needed for optimal results as its absence resulted in a lower yield of 64% (Entry 2). However, the base could be reduced to 0.5 equiv. (Entry 3) or replaced with inorganic salts, such as KOAc (Entry 4), K_2CO_3 (Entry 5) or $KHCO_3$ (Entry 6), without affecting the yield of **2a**. The volume ratio of THF/MeOH could be lowered to 1∶1 (Entry 7) but not to 1∶3 (Entry 8). Importantly, the electrosynthesis was not sensitive to oxygen, as the reaction of **1a** under air afforded **2a** in 93% yield (Entry 9).

The substrates scope was next investigated (Table 2). The reaction was compatible with diphenylamines substituted at the *para*-position of both phenyl rings with Me (**2b**), Ph (**2c**), F (**2d**), Br (**2e**) or I (**2f**). Unsymmetrically *para*-substituted diphenylamines (**2g**～**2i**) and 4-methyl-*N*-phenylaniline (**2j**) bearing an unsubstituted phenyl ring were also viable substrates. However, the reaction of the parent diphenylamine **1k** failed to afford the tetraphenylhydrazine (**2k**). Diarylamines containing a pyridyl ring also underwent efficient dimerization (**2l**). Further investigation revealed that 3,6-disubstituted carbazoles were suitable substrates (**2m** and **2n**). *N*-Alkylanilines also underwent N—N dimerization but required the use of KOAc as the base and a higher reaction temperature (**2o**～**2u**). The electrosynthesis could be scaled up to gram scale as demonstrated for the synthesis of **2b**～**2e**.

A possible reaction mechanism was proposed (Scheme 2). The secondary amine **1** was oxidized on the anode to generate radical cation **I**, which loses a proton to the added base to generate aminyl radical **II**. Homodimerization of **II** affords the tetrasubstituted hydrazine product **2**.[7] At the cathode, MeOH solvent was reduced to generate hydrogen gas and MeO^-. The cathodically generated MeO^- reacts with pyridinium to regenerate MeOH and pyridine. Hence, MeOH and pyridine are not consumed during the electrolysis. Since the oxidation potential of the hydrazine product [$E_{p/2}$(**2a**)=0.68 V vs SCE in MeCN] is lower than that of the starting amine [$E_{p/2}$(**1a**)=0.80 V vs SCE in MeCN], the oxidative dimerization reaction is likely self-catalyzed, *e.g.* the hydrazine product serves as a redox catalyst for the anodic generation of radical cation **I**.

3 Conclusions

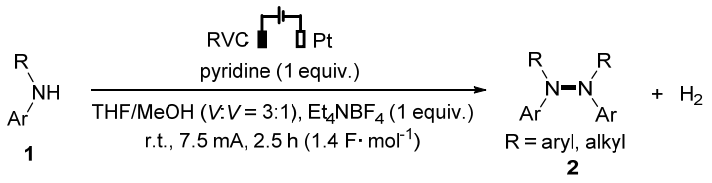
In summary, an electrochemical method for the synthesis of tetrasubstituted hydrazines with diverse electronic properties through dehydrogenative homodimerization of secondary arylamines has developed. The reactions do not need oxidizing reagents and transition metal catalysts and can be carried out efficiently on gram scale.

4 Experimental section

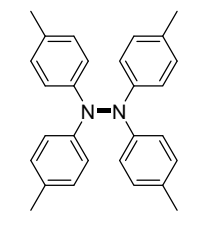
4.1 General information

Anhydrous tetrahydrofuran was obtained from sodium/benzophenone by distillation under argon. Flash column chromtography was performed with silica gel (230～400 mesh). NMR spectra were recorded on a Bruker AV-500 instruments. High resolution mass spectra (ESI HRMS) were recorded on a Micromass QTOF2 Quadruple/Time-of-Flight Tandem mass spectrometer by the

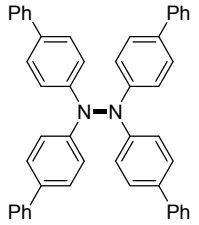
Table 2 Scope of electrochemical synthesis of tetrasubstituted hydrazines[a]



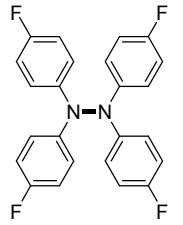
1 **2**



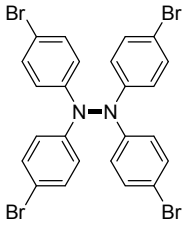
2b, 84% (80%, 0.94 g)[b]



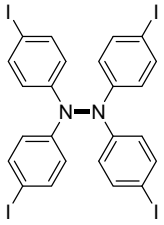
2c, 90% (85%, 1.6 g)[b]



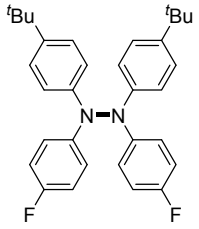
2d, 90% (87%, 0.94 g)[b]



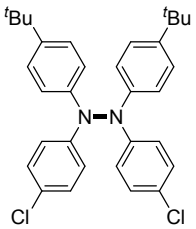
2e, 95% (88%, 1.7 g)[b]



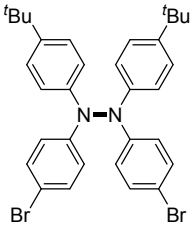
2f, 84%



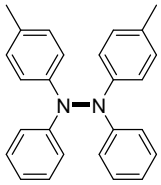
2g, 72%



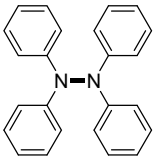
2h, 90%



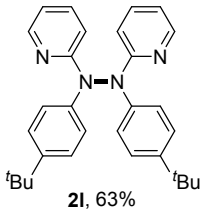
2i, 89%



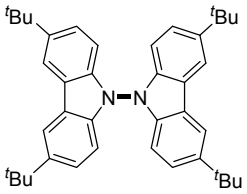
2j, 73%



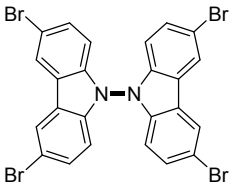
2k, 0%



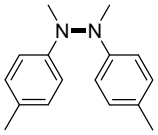
2l, 63%



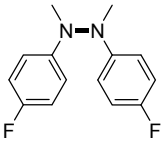
2m, 57%



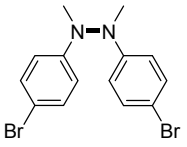
2n, 75%



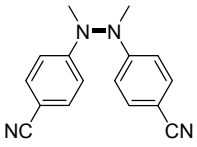
2o, 67%[c]



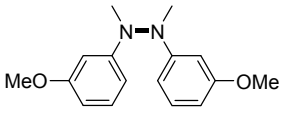
2p, 58%[c]



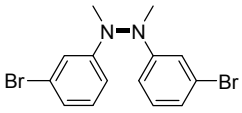
2q, 69%[c]



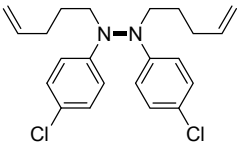
2r, 84%[c]



2s, 70%[c]

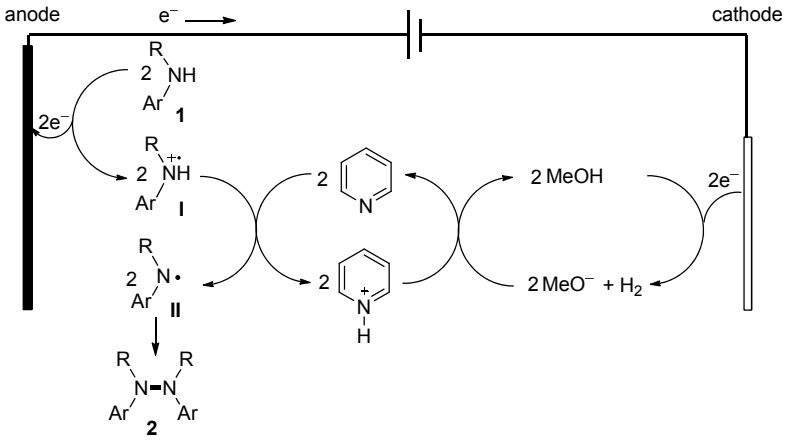


2t, 36%[c]



2u, 61%[c]

[a] Reaction conditions: **1** (0.5 mmol), pyridine (0.5 mmol), Et_4NBF_4 (0.5 mmol), MeOH (2.5 mL), THF (7.5 mL), r.t., 2.5～3 h (1.4～1.7 F•mol^{-1}). [b] **1** (6 mmol), pyridine (6 mmol), Et_4NBF_4 (6 mmol), MeOH (30 mL), THF (90 mL), reflux, 70 mA, 2.5 h (1.1 F•mol^{-1}). [c] Reaction under reflux using KOAc (1 equiv.) as the base.



Scheme 2 Proposed mechanism for the electrochemical synthesis of tetrasubstituted hydrazines

instrumentation center of Department of Chemistry, Xiamen University. Cyclic voltammograms were obtained on a CHI 760E potentiostat. Infrared spectra (IR) and melting point (m.p.) were recorded on a Nicolet-Avater 330 spectrometer and BUCHI melting point M-560, respectively.

4.2 General procedure for the electrolysis

A 25 mL three-necked round-bottomed flask was charged with substrate (0.5 mmol), Et_4NBF_4 (0.5 mmol) and pyridine (0.5 mmol). The flask was equipped with a reticulated vitreous carbon (100 PPI, 1.0 cm×1.0 cm×1.2 cm) anode, a platinum plate (1 cm×1 cm) cathode and then flushed with argon. The electrodes were fixed on the flask using thermometer adaptors. THF (7.5 mL) and MeOH (2.5 mL) were added. The electrolysis was carried out at room temperature using a constant current of 7.5 mA until complete consumption of the substrate (monitored by TLC or ^{1}H NMR). For the synthesis of compounds **2o**～**2u**, the reactions were conducted under reflux (oil bath temperature set at 80 ℃) employing KOAc (0.5 mmol) as the base. The reaction mixture was concentrated under reduced pressure, and the residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product.

The gram scale synthesis of **2b**～**2e** was conducted in a 250 mL beaker-type cell with a RVC (3.4 cm×3.4 cm×1.2 cm) anode, a Pt plate cathode (3 cm×3 cm), and a constant current of 70 mA. The reaction mixture consisted substrate (6.0 mmol), Et_4NBF_4 (1.3 g, 6.0 mmol), pyridine (0.47 g, 6.0 mmol), THF (90 mL) and MeOH (30 mL).

4.3 Characterization data for new compounds

1,1,2,2-Tetra([1,1'-biphenyl]-4-yl)hydrazine (**2c**): Yield 90%, gram scale yield 85%, yellow solid. m.p. 119.1～120.4 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54 (d, J=7.7 Hz, 8H), 7.51 (d, J=8.5 Hz, 8H), 7.47 (d, J=8.5 Hz, 8H), 7.39 (t, J=7.7 Hz, 8H), 7.30～7.26 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 142.8, 140.6, 135.3, 128.9, 128.0, 127.0, 126.7, 118.7; IR (KBr) v: 1601, 1518, 1485, 1320, 760 cm^{-1}; HRMS (ESI) calcd for $C_{48}H_{36}N_2Na$ $[M+Na]^+$ 663.2771, found 663.2770.

1,1,2,2-Tetrakis(4-iodophenyl)hydrazine (**2f**): Yield 84%, white solid. m.p. 130.2～132.0 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, J=8.4 Hz, 8H), 6.96 (d, J=8.4 Hz, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 142.4, 138.5, 120.2, 85.6; IR (KBr) v: 1576, 1484, 1316, 1290, 1180, 809 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}I_4N_2Na$ $[M+Na]^+$ 862.7384, found 862.7398.

1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-bis(4-fluorophenyl)hydrazine (**2g**): Yield 72%, light yellow solid. m.p. 74.1～74.3 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23～7.21 (m, 4H), 7.21～7.18 (m, 4H), 7.17～7.12 (m, 4H), 6.91～6.84 (m, 4H), 1.26 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.3 (d, J_{C-F}=240.7 Hz), 144.8, 141.4, 140.2 (d, J_{C-F}=2.6 Hz), 126.2, 119.9 (d, J_{C-F}=7.8 Hz), 117.3, 115.9 (d, J_{C-F}=22.6 Hz), 34.3, 31.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −121.5; IR (KBr) v: 1504, 1318, 1226, 1134, 1080, 822 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{34}F_2N_2Na$ $[M+Na]^+$ 507.2582, found 507.2583.

1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-bis(4-chlorophenyl)-hydrazine (**2h**): Yield 90%, brown solid. m.p. 134.2～136.6 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24～7.20 (m, 4H), 7.20～7.14 (m, 8H), 7.14～7.10 (m, 4H), 1.26 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 145.8, 142.7, 140.5, 129.3, 126.3 (2C), 118.8, 118.3, 34.4, 31.5; IR (KBr) v: 1591, 1487, 1318, 1095, 819 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{34}Cl_2N_2Na$ $[M+Na]^+$ 539.1991, found 539.1995.

1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-bis(4-bromophenyl)-hydrazine (**2i**): Yield 89%, light yellow solid. m.p. 100.0～101.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.26 (d, J=6.9 Hz, 4H), 7.23～7.20 (m, 4H), 7.19～7.16 (m, 4H), 7.13～7.09 (m, 4H), 1.27 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 145.9, 143.2, 140.3, 132.2, 126.3, 119.1, 118.4, 113.7, 34.4, 31.5; IR (KBr) v: 1584, 1484, 1317, 1134, 1079, 818 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{34}Br_2N_2Na$ $[M+Na]^+$ 629.0960, found 629.0959.

1,2-Bis(4-(*tert*-butyl)phenyl)-1,2-di(pyridin-2-yl)hydrazine (**2l**): Yield 63%, light yellow sticky solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.26 (ddd, J=4.9, 2.0, 1.0 Hz, 2H), 7.46～7.42 (m, 4H), 7.27 (s, 2H), 6.95 (dd, J=8.5, 1.0 Hz, 2H), 6.78 (ddd, J=7.3, 4.9, 1.0 Hz, 2H), 1.27 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.7, 148.0, 146.4, 139.5, 138.3, 125.8, 120.0, 116.7, 110.6, 34.4, 31.6; IR (KBr) v: 1587, 1512, 1468, 1429, 1331 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{35}N_4$ $[M+H]^+$ 451.2856, found 451.2861.

3,3',6,6'-Tetra-*tert*-butyl-9,9'-bicarbazole (**2m**): Yield 57%; White solid; m.p. 263.4～266.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.18 (d, J=1.7 Hz, 4H), 7.31～7.25 (m, 4H), 6.71 (d, J=8.5 Hz, 4H), 1.43 (s, 36H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.1, 138.6, 124.2, 122.0, 116.6, 108.8, 35.0, 32.2; IR (KBr) v: 1632, 1486, 1397, 1031, 787 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{48}N_2Na$ $[M+Na]^+$ 579.3710, found 579.3708.

1,2-Bis(4-fluorophenyl)-1,2-dimethylhydrazine (**2p**): Yield 58%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.00～6.90 (m, 4H), 6.82～6.75 (m, 4H), 2.91 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.9 (d, J_{C-F}=237.0 Hz), 145.6 (d, J_{C-F}=1.8 Hz), 115.8 (d, J_{C-F}=22.3 Hz), 113.90 (d, J_{C-F}=7.4 Hz), 33.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −126.9; IR (KBr) v: 2921, 1505, 1225, 1139, 1098, 823 cm^{-1}; HRMS (APCI) calcd for $C_{14}H_{15}F_2N_2$ $[M+H]^+$ 249.1198, found 249.1205.

1,2-Bis(3-bromophenyl)-1,2-dimethylhydrazine (**2t**): Yield 36%, white solid. m.p. 93.1～93.8 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.09 (t, J=8.2 Hz, 2H), 7.01～6.91 (m, 4H), 6.71 (ddd, J=8.2, 2.4, 0.9 Hz, 2H), 2.97 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 150.1, 130.8, 123.8, 122.0, 115.6, 111.3, 34.2; IR (KBr) v: 2919, 1587, 1481, 1275, 1029, 750 cm^{-1}; HRMS (APCI) calcd for $C_{14}H_{14}Br_2N_2Na$ $[M+Na]^+$ 390.9416, found 390.9420.

1,2-Bis(4-chlorophenyl)-1,2-di(pent-4-en-1-yl)hydrazine (**2u**): Yield 61%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.17～7.11 (m, 4H), 6.63～6.59 (m, 4H), 5.78 (ddt, J=16.9, 10.2, 6.7 Hz, 2H), 5.05～4.97 (m, 4H), 3.38 (t, J=8.0 Hz, 4H), 2.08 (qt, J=7.3, 1.4 Hz, 4H), 1.83～1.70 (m,

4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 146.9, 137.6, 129.3, 123.4, 115.7, 113.9, 50.5, 31.5, 27.1; IR (KBr) ν: 2921, 1592, 1492, 1384, 1277, 1096, 816 cm^{-1}; HRMS (APCI) calcd for $C_{22}H_{27}Cl_2N_2$ $[M+H]^+$ 389.1546, found 389.1548.

Supporting Information Cyclic voltammograms and NMR spectra of new compounds. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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