Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Novel hole transport materials based on *N,N'*-disubstituted-dihydrophenazine derivatives for electroluminescent diodes

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Content

1. Synthetic procedure of intermediates 3-11

***N*-(4-bromophenyl)-*N*-phenylnaphthalen-1-amine (3):** N-phenylnaphthalen-1-amine (10 g, 45.6 mmol), 1-bromo-4-iodobenzene (12.86 g, 45.6 mmol), copper iodide (1.74 g, 9.1 mmol), potassium hydroxide (5.1 g, 9.1 mmol), 1,10-phenanthroline monohydrate (1.8 g, 9.1 mmol) and 1,2-dimethylbenzene (50 mL) were added to a 100 mL two-necked round-bottomed flask. The mixture was heated to 220 ºC for 15 h. Water (10 mL) was added to stop the reaction, and then the mixture was extracted with dichloromethane (3×30 mL). The organic layer was dried with $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash column chromatography by using petroleum ether as the eluent. Viscous liquid; yield: 6.2 g (36%) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, J= 8.5 Hz, 1H), 8.00 (d, J= 8.2 Hz, 1H), 7.89 (d, J= 8.2 Hz, 1H), 7.57 (t, J= 7.7 Hz, 2H), 7.47 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 2H), 7.20 (d, J= 7.7 Hz, 2H), 7.09 (t, J= 7.3 Hz, 1H), 7.04 – 6.98 (m, 2H).

(4-(naphthalen-1-yl(phenyl)amino)phenyl)boronic acid (4): N-(4-bromophenyl)-N-phenylnaphthalen-1-amine (5 g, 13.4 mmol) was dissolved in dry tetrahydrofuran (50 mL). The nBuLi/hexane solution (8.4 mL, 6.7 mmol) was added dropwise at -78 ºC under nitrogen atomphere for 1 h. Then triisopropyl borate (9.3 mL, 134 mmol) was added slowly. The mixture was reacted at -78 ºC for 1 h and then at room temperature overnight. The water was added to stop the reaction and adapt PH to 1-2 by adding 2 M hydrochloric acid. The mixture was extracted with dichloromethane (3×30 mL). The organic layer was dried with $MgSO_4$. The solvent was removed in vacuo and the residue was recrystallized by n-hexane. White solid; yield: 4.40 g, 97%. The product was used to the next step without further purification.

9-(4-bromophenyl)-9H-carbazole (5): 9-(4-bromophenyl)-9H-carbazole was prepared from 9H-carbazole and 1-bromo-4-iodobenzene by the same synthetic procedure as that for N-(4-bromophenyl)-N-phenylnaphthalen-1-amine. White powder, yield: 8.01 g (82.7%). ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.17 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.44 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 7.7 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.32 (d, J = 5.4 Hz, 1H).

(4-(9H-carbazol-9-yl)phenyl)boronic acid (6): (4-(9H-carbazol-9-yl)phenyl)boronic acid was prepared from 9-(4-bromophenyl)-9H-carbazole by the same synthetic procedure as that for (4-(naphthalen-1-yl(phenyl)amino)phenyl)boronic acid. White powder, yield: 1.58 g (89%).

2-(2-nitrophenyl)thiophene (7): A mixed solution of 1-bromo-2-nitrobenzene（3g, 15 mmol) and thiophen-2-ylboronic acid (1.28g, 10 mmol) tetrakis(triphenylphosphine)palladium(0) (0.2 g, 0.172mmol), toluene (20 mL) and 2 N K_2CO_3 aqueous solution (3.75 mL) was heated at 100 ºC with stirring under an argon atmosphere. After 12 h, the mixture was cooled to room temperature. The

mixture was then quenched with water (20 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic phase was dried (anhydrous $MgSO_4$). The solvent was removed in vacuo and the residue was purified by flash column chromatography (petroleum ether: dichloromethane=15:1) to give brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.49 – 7.43 (m, 1H), 7.41 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.12 – 7.03 (m, 2H).

4H-thieno[3,2-b]indole (8): 2-(2-nitrophenyl)thiophene（1g，4.9 mmol）and triphenylphosphine（1.3g, 5.0 mmol）were dissolved in o-xylene (20 mL) and heated to reflux for 10 h. The solvent was removed in vacuo and the residue was washed with petroleu mether and hot water successively. Brown powder, yield: 0.6 g (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 5.2 Hz, 1H), 7.28-7.30(m, 1H), 7.25 – 7.19 (m, 1H), 7.10 (d, J = 5.2 Hz, 1H).

4-bromo-[N-(2-phenylamino)phenyl]benzamide (9):4-bromobenzoic acid (3.0 g, 15 mmol), sulfurous dichloride (5 mL), 1,2-dichloroethane (20 mL) were added in 100 mL one-necked round-bottomed flask and heated to reflux. After 3h, the solvent and sulfurous dichloride was removed in vacuo. Then N^1-phenylbenzene-1, 2-diamine (2.8 g, 15 mmol) and NMP (20 mL) were added and stirred at room temperature overnight. Water was added to stop the reaction and solid was filtered. The crude product was recrystallized by THF and methanol to obtain white solid (3.56 g, 64.8%). ^{1}H NMR (400 MHz, DMSO), δ: 9.78(s,1H), 7.82-7.84(d, J = 8.8 Hz, 2H), 7.68-7.70(d, J = 8.4 Hz, 2H), 7.51-7.53 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.28-7.30(d, J = 8.4 Hz,1H), 7.13-7.20(m, 3H), 6.97-7.01(t, J = 7.6 Hz, 1H), 6.91-6.93 (d, J = 7.6 Hz, 2H), 6.76-6.80(t, J = 7.2 Hz,1H).

2-(4-bromophenyl)-1-phenyl-1H-benzimidazole (10): 4-bromo-[N-(2-phenylamino)phenyl]benzamide (0.7 g, 1.91 mmol) and acetic acid (10 mL) were added in 50 mL one-necked round-bottomed flask and heated for 12h. The solvent was removed and 5 mL methylalcohol was added in refrigerator to get white solid (0.6 g, 90.2 %).^{1}H NMR (400 MHz, DMSO), δ: 7.78-7.81(d, J = 7.6 Hz, 1H), 7.54-7.60(m, 5H), 7.43-7.46(m, 4H), 7.26-7.34(m, 2H), 7.17-7.19(d, J = 7.2 Hz, 1H).

(4-(1-phenyl-1H-benzo[d]imidazol-2-yl) phenyl)boronic acid (11): 2-(4-bromophenyl)-1-phenyl-1*H*-benzimidazole (2 g, 5.75 mmol) was dissolved in dry tetrahydrofuran (30 mL). The nBuLi/hexane solution (5.4 mL, 8.6 mmol) was added dropwise at -78 ºC under nitrogen atomphere for 1h. Then triisopropyl borate (1.62 g, 8.6 mmol) was added slowly. The mixture was reacted at -78 ºC for 1 h and then at room temperature overnight. The water was added to stop the reaction and adapt PH to 1-2 by adding 2 M hydrochloric acid. The mixture was extracted with dichloromethane (3×30 mL). The organic layer was dried with $MgSO_4$. The solvent was removed in vacuo and the residue was recrystallized by n-hexane. White solid; yield: 1.05 g (58.3%). The product was used to the next step without further

purification.

2. ^{1}H NMR

2.1 ^{1}H NMR of a

2.2 ^{1}H NMR of b

2.3 ^{1}H NMR of c

2.4 ^{1}H NMR of d

2.5 ^{1}H NMR of e

2.6 ^{1}H NMR of f

2.7 ^{1}H NMR of g

2.8 ^{1}H NMR of h

2.9 ^{1}H NMR of i

3. ^{13}C NMR

3.1 ^{13}C NMR of a

3.2 ^{13}C NMR of b

3.3 ^{13}C NMR of c

3.4 ^{13}C NMR of d

3.5 ^{13}C NMR of e

3.6 ^{13}C NMR of f

3.7 ^{13}C NMR of g

3.8 ^{13}C NMR of h

3.9 ^{13}C NMR of i

4. Mass spectrometry

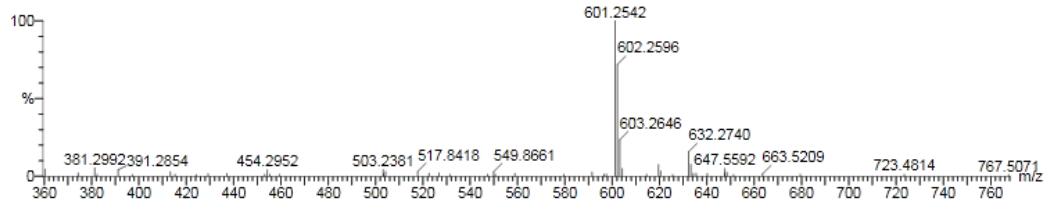
4.1 Mass spectrometry of a

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
29 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-48 H: 0-100 N: 0-3

JH-SU ECUST institute of Fine Chem 23-Oct-2013 16:24:38
TH-ZZZ-111 64 (0.483) Cm (64:68) 1: TOF MS ES+ 1.28e+004



Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
602.2596	602.2596	0.0	0.0	30.5	17.1	0.0	C44 H32 N3

4.2 Mass spectrometry of b

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
17 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-50 H: 0-100 N: 0-3

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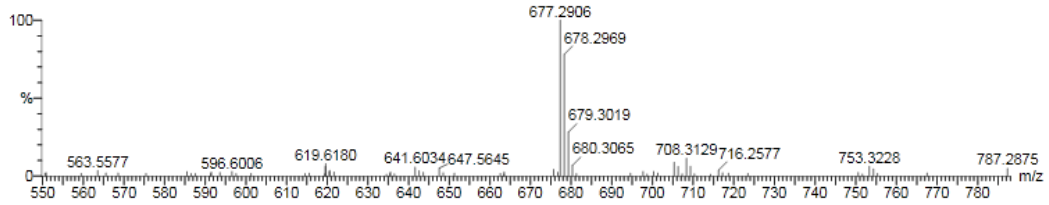

Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
678.2969	678.2909	6.0	8.8	34.5	17.3	0.0	C50 H36 N3

4.3 Mass spectrometry of c

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
18 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-48 H: 0-100 N: 0-3

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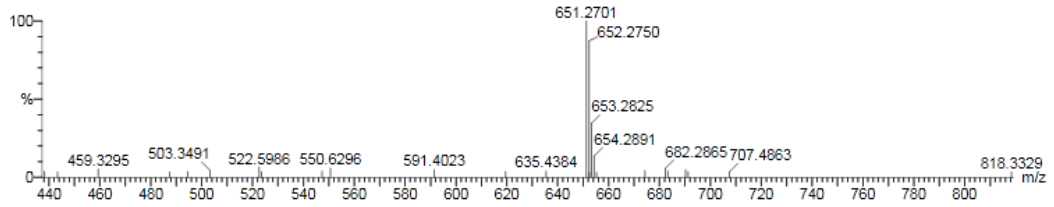

Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
652.2750	652.2753	-0.3	-0.5	33.5	23.4	0.0	C48 H34 N3

4.4 Mass spectrometry of d

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-55 H: 0-50 N: 0-5

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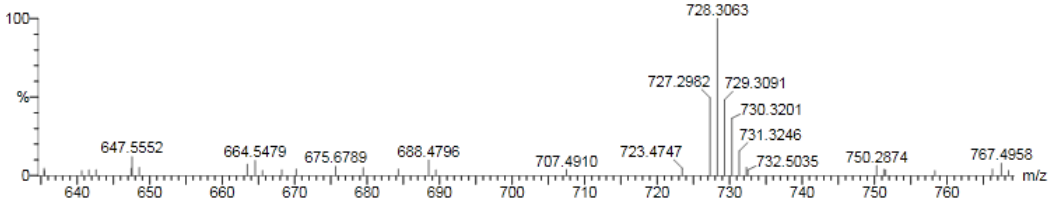

Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
728.3063	728.3066	-0.3	-0.4	37.5	15.1	0.0	C54 H38 N3

4.5 Mass spectrometry of e

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
26 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-55 H: 0-50 N: 0-5

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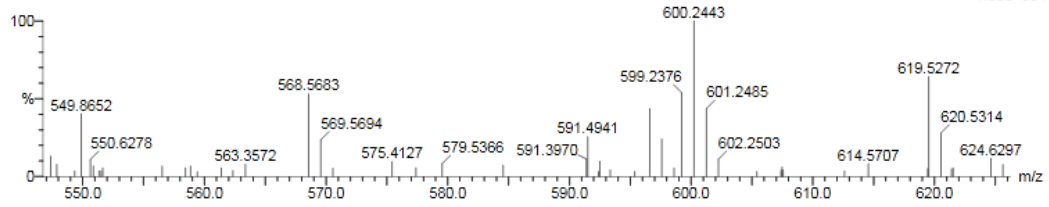

Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
600.2443	600.2440	0.3	0.5	31.5	13.8	0.0	C44 H30 N3

4.6 Mass spectrometry of f

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
130 formula(e) evaluated with 13 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 S: 0-4

TIAN-H ECUST institute of Fine Chem 25-Nov-2013 20:37:51
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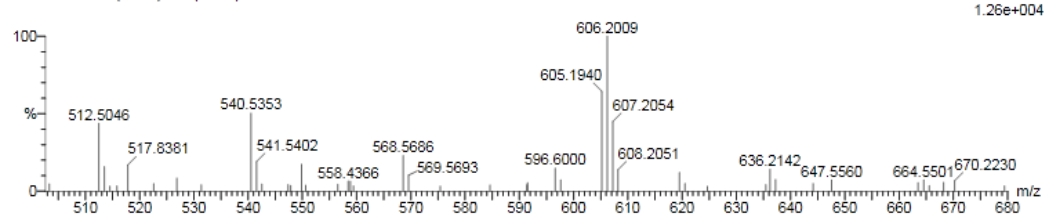

Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
606.2009	606.2004	0.5	0.8	30.5	12.7	0.0	C42 H28 N3 S

4.7 Mass spectrometry of g

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
43 formula(e) evaluated with 4 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-4

JH-SU ECUST institute of Fine Chem 23-Oct-2013 16:13:25
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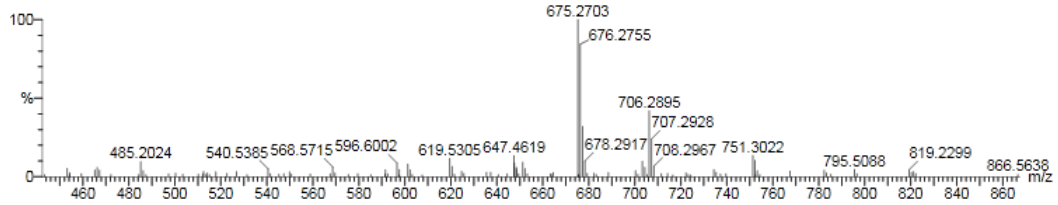

Minimum:				-1.5				
Maximum:		30.0	50.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
676.2755	676.2753	0.2	0.3	35.5	18.7	0.0	C50 H34 N3	

4.8 Mass spectrometry of h

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-60 H: 0-40 N: 0-5

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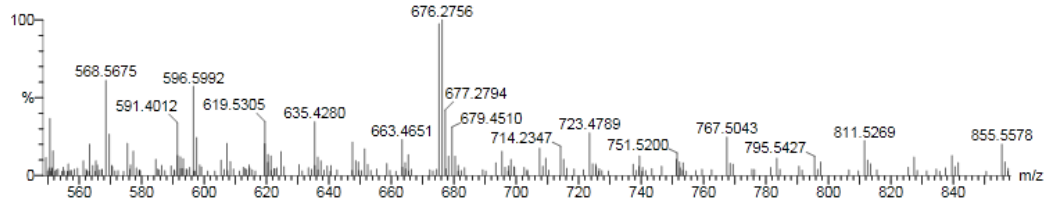
TH-ZZZ-910 134 (0.928) Cm (119:135) 1: TOF MS ES+ 2.09e+003



Minimum:				-1.5				
Maximum:		30.0	50.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
676.2756	676.2753	0.3	0.4	35.5	21.4	0.0	C50 H34 N3	

4.9 Mass spectrometry of i

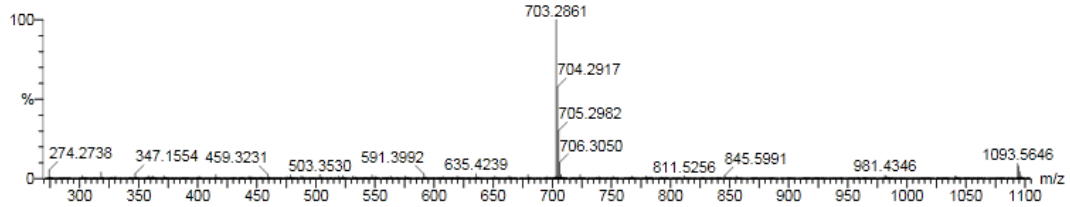
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
31 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-60 H: 0-40 N: 0-8

H-TIAN ECUST institute of Fine Chem 29-Nov-2013 21:35:42

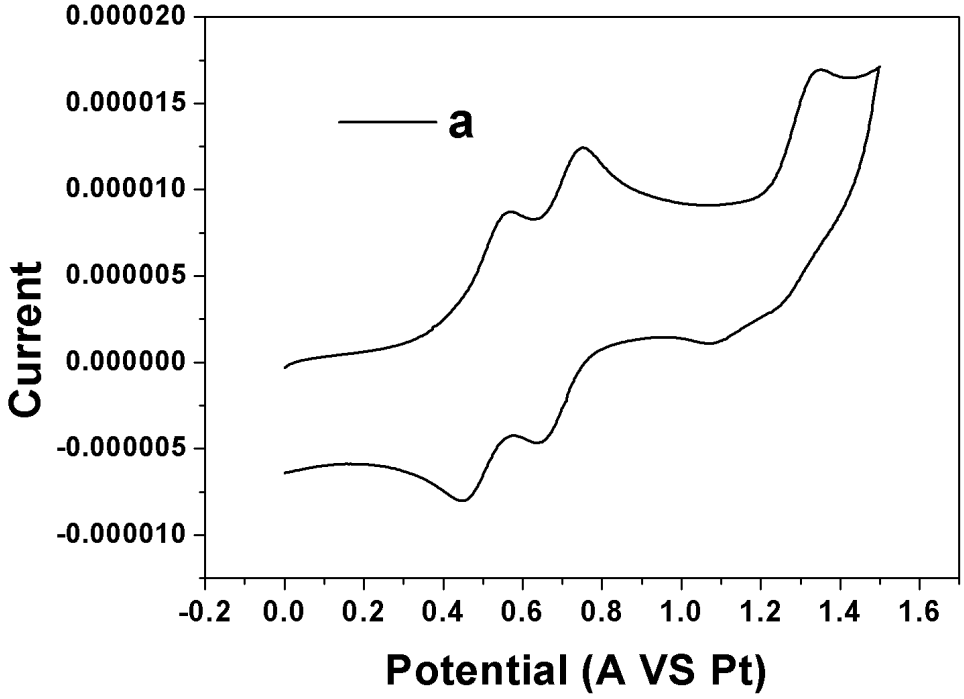
TH-ZZZ-555 68 (0.512) Cm (67:88) 1: TOF MS ES+ 1.19e+004



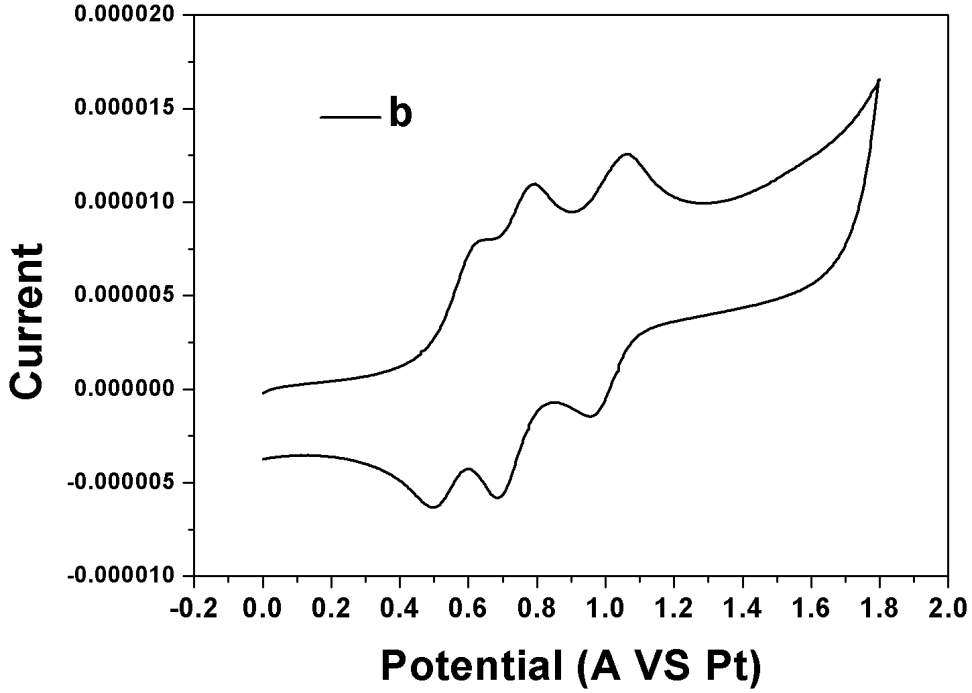
Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
703.2861	703.2862	-0.1	-0.1	36.5	190.4	0.0	C51 H35 N4

5. Electrochemistry of a-i

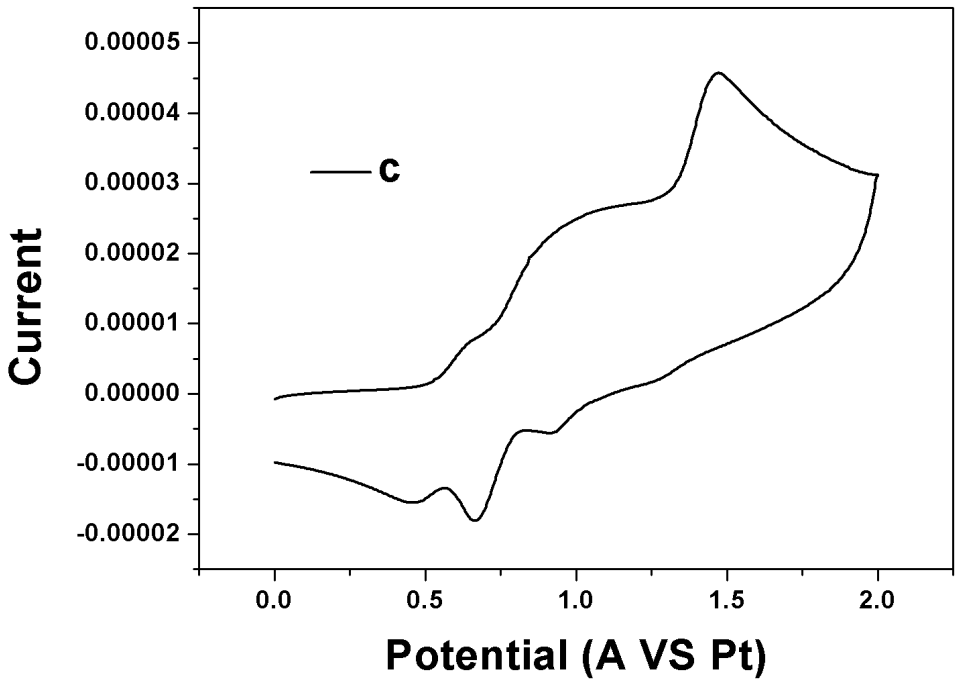
5.1 Electrochemistry of a



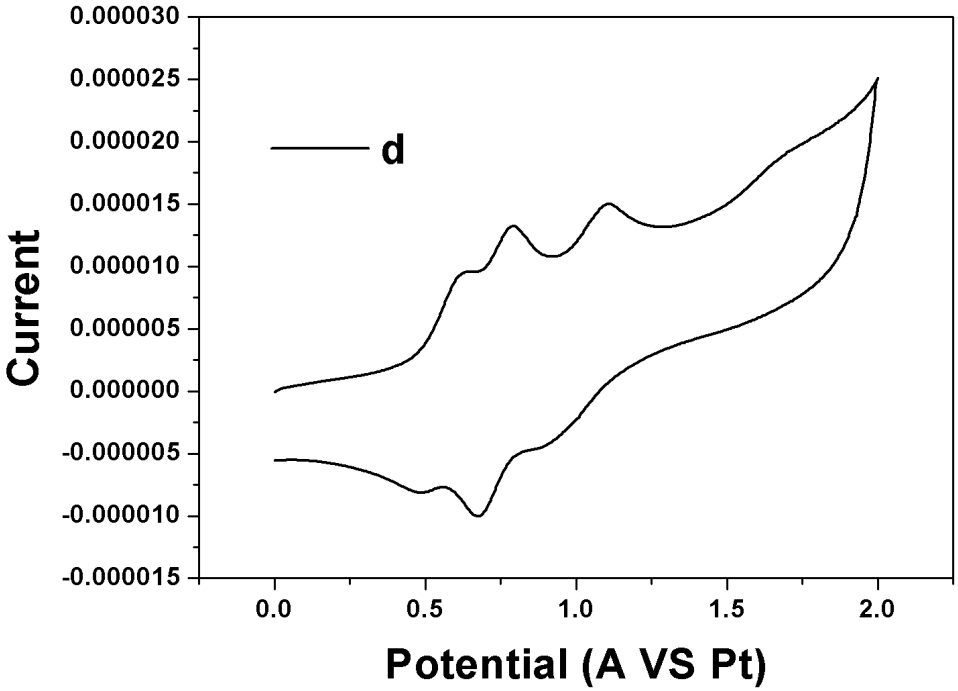
5.2 Electrochemistry of b



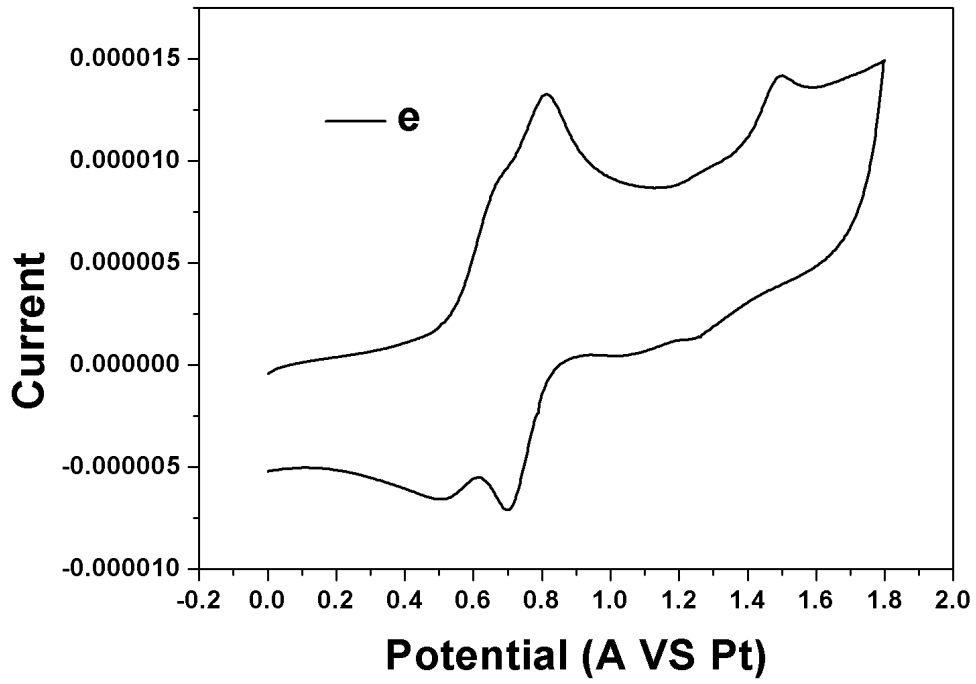
5.3 Electrochemistry of c



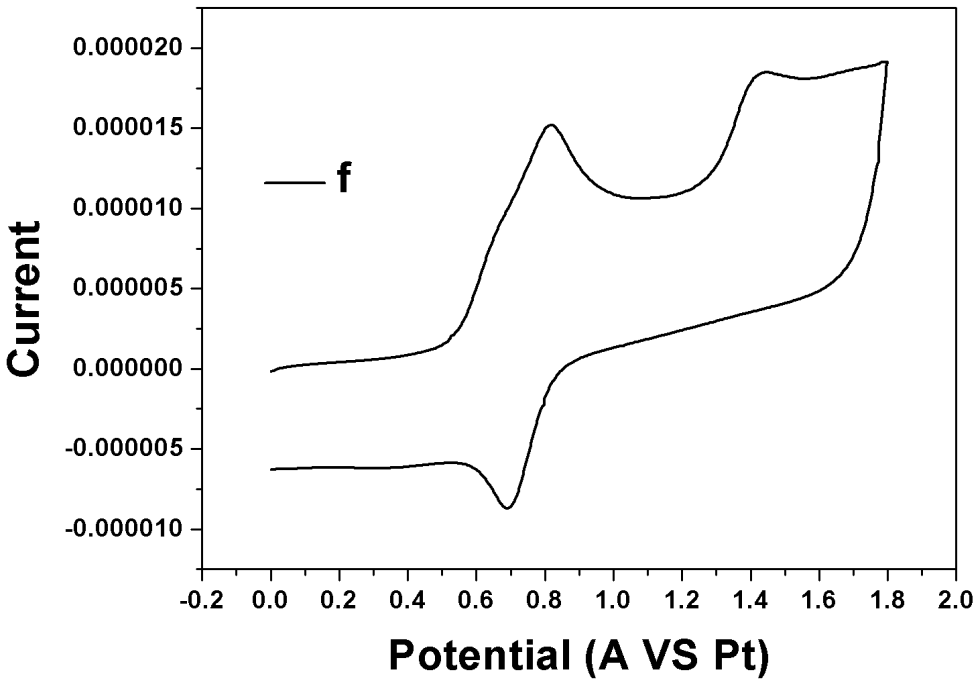
5.4 Electrochemistry of d



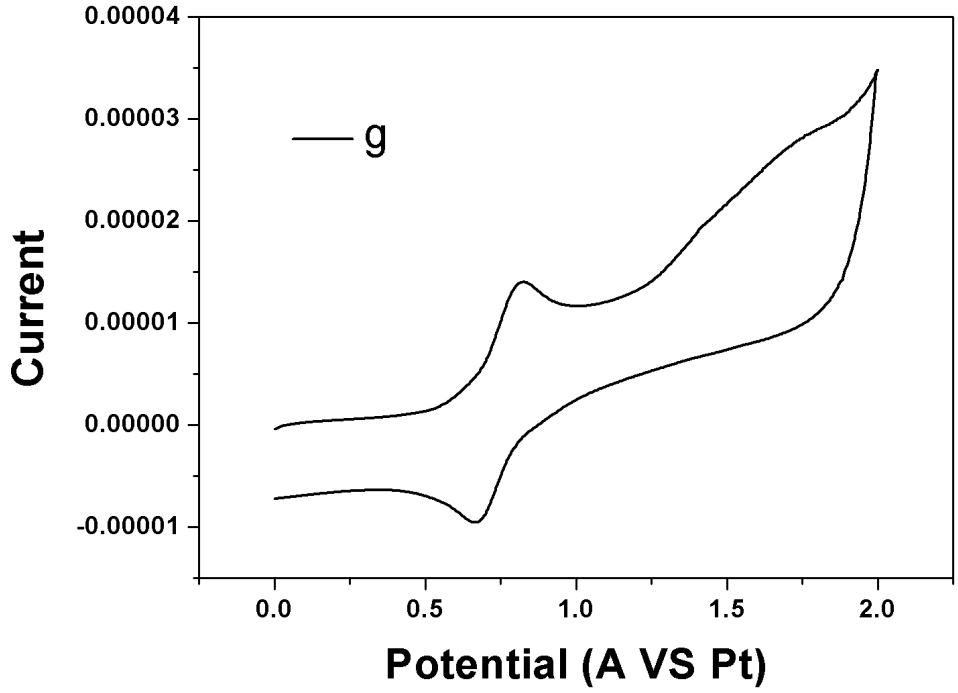
5.5 Electrochemistry of e



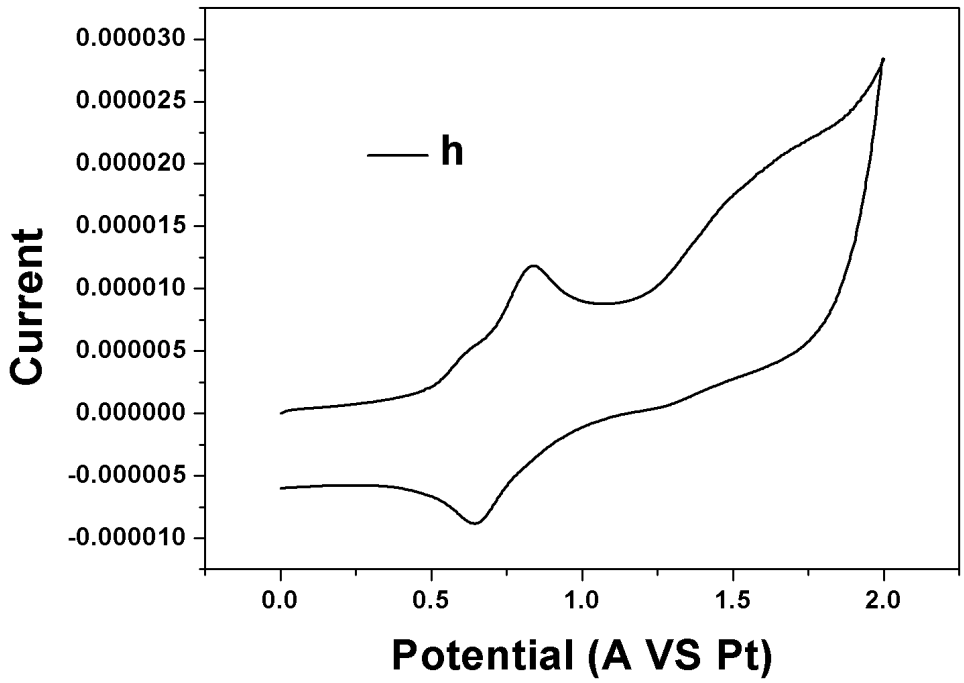
5.6 Electrochemistry of f



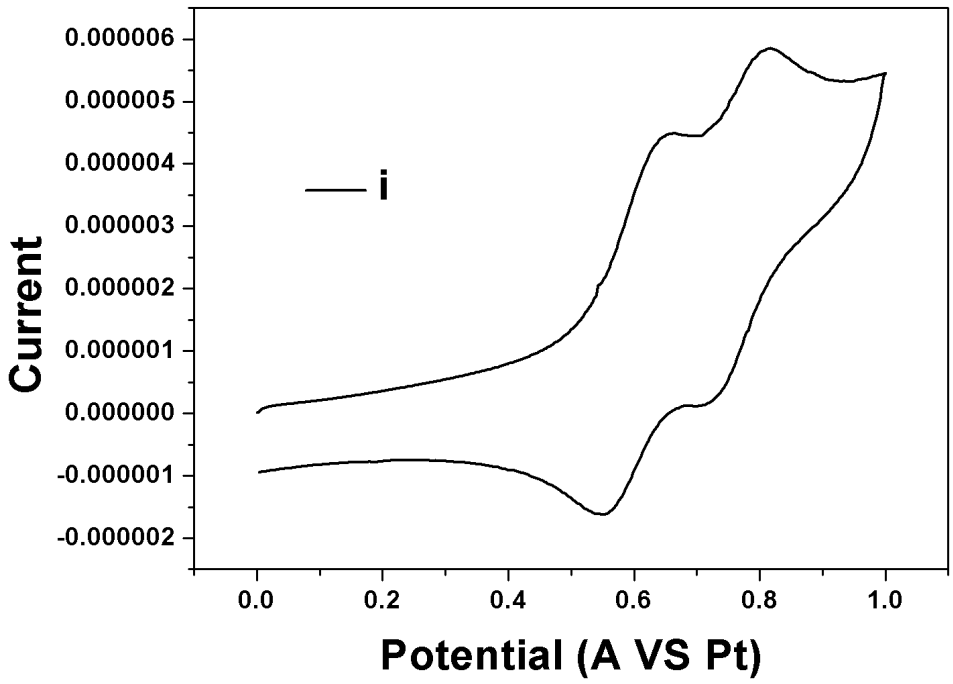
5.7 Electrochemistry of g



5.8 Electrochemistry of h



5.9 Electrochemistry of i



6. X-ray crystallography

	a	e	i
empirical formula	$C_{44}H_{31}N_3$	$C_{45}H_{31}ClN_3$	$C_{52}H_{36}Cl_2N_4$
formula weight	601.72	649.18	787.75
temperature	140(2) K	140(2) K	140(2) K
wavelength, Å	0.71073	0.71073	0.71073
crystal system	Triclinic	Triclinic	Triclinic
space group	P -1	P -1	P -1
a, Å	9.5653(13)	9.322(5)	9.4937(15)
b, Å	11.8383(16)	12.934(7)	10.0154(16)
c, Å	14.678 (2)	14.662(8)	21.812(4)
α（deg）	102.839(3)	75.264(9)	101.429(4)
β（deg）	96.717(3)	81.913(10)	97.164(5)
γ（deg）	102.722(3)	71.406(11)	104.122(3)
V(Å^3)	1556.5(4)	1616.9(16)	1938.5(6)
Z	2	2	2
D_{calcd}(g cm $^{-3}$)	1.284	1.333	1.350
μ(mm^{-1})	0.075	0.158	0.212
***F*(000)**	632	678	820
θ range(deg)	1.824 to 30.647	1.704 to 25.999	0.969 to 30.698
reflections collected	15907	11776	19691
independent reflections	9511	6345	11817
R_{int}	0.0414	0.0857	0.0651
R1, wR2[I>2.0σ(I)]	0.0604, 0.1189	0.0729, 0.1722	0.0755, 0.1931
R1, wR2(all data)	0.1262, 0.1466	0.1697, 0.2258	0.1312, 0.2283
GoF on F^2	0.946	0.962	0.962

7. Thermal property of a-i