Arylated Mono- and Bifunctional 2-Aminothiophenes and 2-Aminothiazoles as a New Class of Hole Transport Materials

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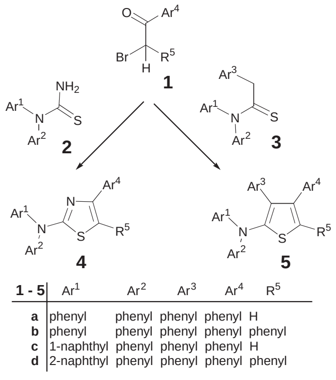
(Received March 18, 2002; CL-020253)

By using the well-known Hantzsch method and starting from some mono- and bifunctional aryl-substituted thioureas, thioacetamides, and bromoketones several new aryl-substituted 2-aminothiazoles and 2-aminothiophenes have been prepared and tested as hole transport materials for OLEDs.

In the last time several aryl-substituted thiophenes received an increasing interest as building block for oligomers and polymers with a tunable electric conductivity.[1] Usually, these compounds were prepared by heavy metal-catalysed coupling reactions of simple thiophenes with halo-substituted benzenes.[2] Although these methods give rise, in common, to high yields of products they are generally contaminated by traces of the heavy metal catalyst. Because traces of heavy-metals have, however, a negative influence on the electric and optical properties of the products their separation is urgently necessary to make them suitable for technical uses. Of course, this procedure is, in common, a time-consuming procedure which raises the price of products significantly.

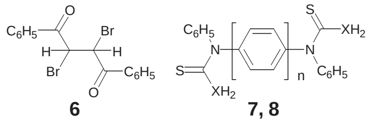
Now we will report on a simple, heavy metal-free route to aryl-substituted 2-aminothiophenes and 2-aminothiazoles which also can serve to produce versatile building blocks for new materials with a high electric conductivity. This synthetic route uses the well-known Hantzsch method and starts from simply available aryl-substituted thioureas, thioacetamides, and haloketones.[3] Thus, aryl-substituted 2-aminothiazoles of the general structure **4** were prepared by starting from corresponding aryl-substituted thioureas **2** and aryl-substituted 2-bromoethanones **1**. Analogously, aryl-substituted 2-aminothiophenes **5** were prepared from the same haloketones **1** and aryl-substituted thioacetamides **3** according to an earlier reported method.[4]



1 - 5	Ar^1	Ar^2	Ar^3	Ar^4	R^5
a	phenyl	phenyl	phenyl	phenyl	H
b	phenyl	phenyl	phenyl	phenyl	phenyl
c	1-naphthyl	phenyl	phenyl	phenyl	H
d	2-naphthyl	phenyl	phenyl	phenyl	phenyl

Scheme 1.

For receiving high yields of products special reaction conditions have to be applied. Thus, the aryl-substituted 2-aminothiazoles **4** are available by heating of the corresponding educts **1** and **2** in ethanol or DMF. The aryl-substituted 2-aminothiophenes **5** are available by allowing to react the aryl substituted thioacetamides **3** with the bromoketones **1** in acetic anhydride at room temperature followed by gentle heating of the reaction mixture with triethylamine. The sulphur-containing starting materials **2** and **3** were prepared by reported methods for thioureas[5] and thioacetamides.[6]

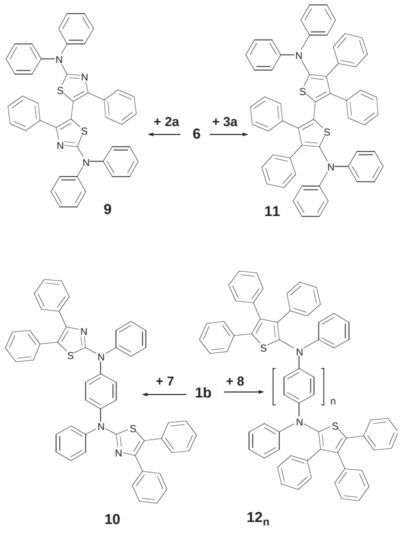


	n	X
7	1	N
8a	1	CC_6H_5
8b	2	CC_6H_5

Scheme 2.

The described method can also be applied, as we found, for the synthesis of arylated bis(2-aminothiazoles) **9** and **10** as well as for arylated bis(2-aminothiophenes) **11** and **12**. To this, the bromoketone **6**,[7] the bifunctional thiourea **7** and the thioacetamide **8** were used. The last-mentioned compounds can be prepared analogously to their monofunctional derivatives **2** and **3** according to reported methods for simple precursors.[8] Their transformation into corresponding products was performed in the same way as described for the synthesis of the mono-heterocyclic compounds **4** and **5** by heating of the required components in a polar solvent in presence of triethylamine.

The new 2-aminothioazoles and 2-aminothiophenes **4**, **5**, and **9**–**12** prepared have been characterized by elemental analysis, mass spectrometry, and NMR spectroscopy.[9] For selected data see Table 1.



Scheme 3.

All heterocyclic compounds **4**, **5**, and **9**–**12** exhibit, as demonstrated by DSC and cyclic voltammetry, a high tendency to form amorphous glasses after cooling their melts and low oxidation potentials. Reversible potentials were found, however, only with the compounds **9**–**12**. This means, that under the applied conditions the radical cations formed from the monoheterocyclic compounds **4** and **5** are less stable. They can dimerise giving rise to the formation of corresponding bithiazoles or bithiophenes as will be demonstrated in detail in a forthcoming paper.

Table 1. Some characteristic substance data of the compounds prepared ($Ar^2 = Ar^3 = Ar^4$ = phenyl)

Nr	Ar^1	R^5	Yield/%	$T_\mathrm{m}{}^\mathrm{a}$/°C	$T_\mathrm{d}{}^\mathrm{a}$/°C	$T_\mathrm{g}{}^\mathrm{a}$/°C	Type$^\mathrm{b}$	$E_\mathrm{ox}{}^\mathrm{c}$/V	ΔE^d/eV	Formula	Mass spectrum$^\mathrm{e}$
4b	phenyl	phenyl	82	223	268	—	A	1.14 (ir)	4.03	$C_{27}H_{20}N_2S$	405.4 (MH^+, 100%)
5a	phenyl	H	67	102	230	20	C	1.00 (ir)	4.61	$C_{26}H_{21}NS$	404.3 (MH^+, 100%)
5b	phenyl	phenyl	60	180	434	57	B	0.95 (r)	3.86	$C_{34}H_{25}NS$	479.3 (MH^+, 100%)
5c	1-naphthyl	H	51	64	252	51	C	1.10 (ir)	4.12	$C_{32}H_{23}NS$	454.4 (MH^+, 100%)
5d	2-naphthyl	phenyl	88	198	330	61	B	0.73 (r)	3.83	$C_{38}H_{27}NS$	529.4 (MH^+, 100%)
9		—	63	232	391	72	B	0.95 (qr), 1.00 (qr)	4.52	$C_{42}H_{30}N_4S_2$	655.4 (MH^+, 100%)
10		phenyl	53	302	418	91	B	1.01 (r), 1.23 (qr)	4.00	$C_{48}H_{34}N_4S_2$	731.4 (MH^+, 100%)
11		—	37	262	368	87	B	0.64 (r)	3.90	$C_{56}H_{40}N_2S_2$	804.5 (M^+, 100%)
$\mathbf{12_1a}$		H	45	263	283	83	B	0.75 (qr), 1.13 (qr)	4.23	$C_{50}H_{36}N_2S_2$	728.3 (M^+, 100%)
$\mathbf{12_1b}$		phenyl	65	317	410	118	B	0,75 (r), 1.07 (r)	3.83	$C_{62}H_{44}N_2S_2$	880.5 (M^+, 100%)
$\mathbf{12_2b}$		phenyl	71	276	431	114	B	0.94 (qr)	3.94	$C_{68}H_{48}N_2S_2$	956.5 (M^+, 100%)
1-Naphdata				247	448	117	C	0.52 (r), 0.76 (r)			
NPD$^\mathrm{f}$				281	327	99	B	0.85 (r), 1.04 (r)			
TPD$^\mathrm{g}$				173	367	63	C	0.82 (r), 0.95 (r)			

$^\mathrm{a}T_\mathrm{m}$: melting point, T_d: decomposition point, T_g glass transition point. $^\mathrm{b}$Type A: recrystallisation at cooling, Type B: no crystallisation at cooling, recrystallisation above the T_g, Type C: no crystallisation at cooling, no crystallisation above the T_g. $^\mathrm{c}$ir: irreversible potential, qr: quasi reversible potential, r: reversible potential. $^\mathrm{d}$Energy of electronic absorption. $^\mathrm{e}$ESI. $^\mathrm{f}$NPD: *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-[1,1′-biphenenyl]-4,4′-diamine. $^\mathrm{g}$TPD: *N*,*N*′-bis(3-tolyl)-*N*,*N*′-diphenyl-[1,1′-biphenyl]-4,4′-diamine.

The bis-heterocyclic compounds **9**–**12** exhibiting reversible oxidation potentials were checked as hole transport materials in organic light emitting diodes (OLEDs). These have been manufactured by vacuum-evaporation on an ITO-coated glass substrate. The evaporation process was performed at 5×10^{-6} mbar with an evaporation rate of ca. 1–5 Å/s.

The effectiveness of the hole transport ability of the investigated compounds was estimated by measurement of the luminescence of Alq_3 as a function of the applied voltage or currency density and compared with some standard materials, such as 1-Naphdata[10] or α-NPD.[11] Some results of these measurements are depicted in Figure 1.

In Figure 1 the luminance of several OLEDs as a function of the currenr density are shown. For each plot both the sequence of layers and the reached quantum efficiencies @ 1000 cd m^{-2} are listed. For comparison, the plot of an internal standard-device, consisting of an ITO-Anode/Copper-Phthalocyanine (5 nm)/1-Naphdata (55 nm) as hole transport layer (HTM) 1/α-NPD (5 nm) as HTM 2/Alq_3 (60 nm)/LiF (0.5 nm)/Al-cathode (150 nm) is given. The layer-thickness used of HTM 1 was always 55 nm and 5 nm for HTM 2. The maximum of luminance of this OLED is measured as 21 000 cd m^{-2} @ 0.68 A cm^{-2} (~14 V). The maximum of luminance in an OLED with the same thickness of layers and using 1-Naphdata as HTM 1 and compound **10** as HTM 2 is measured as 26 500 cd m^{-2} @ 1.05 A cm^{-2} (~13 V).

Only satisfactory results were obtained with OLEDs manufactured with α-NPD as HTM 1 and $\mathbf{12_2b}$ as HTM 2. An OLED in which both of the standard materials were substituted by the compounds $\mathbf{12_1b}$ and $\mathbf{12_2b}$ exhibit surprisingly a higher luminance efficiency as an OLED manufactured with the standard materials.

These data demonstrate that the *N*-perarylated 2-aminothiophenes and 2-aminothiazoles of the structure **9**–**12** represent a new class of easily oxidizable compounds with a good tendency to form amorphous glasses in which the charged species formed by electrochemical oxidation exhibit a high mobility giving rise to a strong Alq_3 luminescence. They are easily available by a Hantzsch-type reaction from mono-functional or bifunctional aryl-substituted thioureas or thioacetamides and 2-bromoethanones without using of any heavy metal catalyst which are, as mentioned above, implicitly necessary for the synthesis of the most of their carbocyclic analogues, e.g., for α-NPD and 1-Naphdata, or some thiophene-based starburst compounds recently described.[12,13]

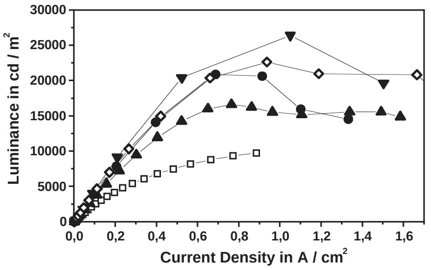


Figure 1. Luminance characteristics and external quantuum efficiencies (q.e.) of some OLEDs manufactured with several hole transport materials, □: $\mathbf{12_1b}$/α-NPD (q.e. 0.79%), ●: 1-Naphdata/α-NPD (q.e. 1.19%), ▲: 1-Naphdata/$\mathbf{12_2b}$ (q.e. 1.05%), ▼: 1-Naphdata/**10** (q.e. 1.30%), ◇: $\mathbf{12_1b}$/$\mathbf{12_2b}$ (q.e. 1.33%).

This work was financially supported by the BMBF and the SIEMENS AG, Erlangen, Germany.

References and Notes

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8 *N*,*N*′-(bis-thiocarbamido)*N*,*N*′-diphenyl-1,4-phenylenediamine **7**, m.p. 177 °C, from 1,4-phenylenediamine via the corresponding *N*,*N*′-bis-(pivaloylthiourea) accordingly to Ref. 5; *N*,*N*′-(bis-phenylthioacetyl)*N*,*N*′-diphenyl-1,4-phenylene diamine **8**, m.p. 223–227 °C, from the corresponding bis-amide accordingly to ref. 6; *N*,*N*′-(bis-phenylthioacetyl)-*N*,*N*′-(diphenyl) benzidine **9**, m.p. 190–194 °C, from the corresponding bis-amide accordingly to Ref. 6.

9 **4a**: ^{13}C NMR ($CDCl_3$, 300 Mz) δ = 126.7, 126.8, 127.2, 128.8, 129.6, 130.6, 134.5, 135.9, 146.3, 152.8, 169.7; **5a**: 120.8, 122.7, 123.3, 127.9, 127.8, 128.9, 129.1, 129.8, 130.0, 130.9, 136.0, 138.0, 138.4, 142.6, 147.3, 148.6; **5b**: 122.5, 123.0, 127.2, 127.3, 127.8, 128.1, 128.5, 129.1, 129.5, 130.0, 130.5, 131.6, 135.1, 135.8, 136.4, 136.9, 137.9, 140.1, 145.1, 148.1; **5c**: 118.9, 120.1, 121.3, 125.5, 126.6, 126.7, 126.8, 127.0, 127.5, 127.6, 127.8, 128.9, 129.0, 129.1, 129.8, 129.9, 131.1, 131.2, 135.9, 136.3, 137.8, 138.0, 142.6, 143,8, 148.4, 151.3; **5d**: 118.6, 122.7, 122.9, 123.2, 125.0, 126.9, 127.2, 127.4, 127.7, 127.9, 128.1, 128.2, 128.6, 128.9, 129.2, 129.6, 130.0, 130.4, 130.5, 131.6, 134.9, 135.1, 135.8, 136.5, 136.8, 138.0, 140.2, 145.0, 145.8, 148.0, **9**: 113.8, 126.9, 128.8, 129.2, 129.3, 129.4, 130.6, 135.6, 141.7, 145.8, 150.8; **10**: 124.0, 125.6, 126.8, 127.3, 128.0, 128.4, 128.8, 129.4, 129.5, 130.6, 132.3, 135.3,141.7, 144.6, 145.9, 162.3, 165.7; **11**: 121.5, 122.1, 126.5, 126.6, 127.4, 127.8, 128.7, 128.8, 129.7, 130.6, 134.7, 135.4, 137.9, 140.9, 145.7, 147.0; $\mathbf{12_1a}$: 119.3, 120.0, 121.3, 123.8, 126.8, 126.9, 127.9, 128.1, 128.8, 130.0, 135.1, 136.8, 136.9, 141.6, 142.1, 146.8, 148.2; $\mathbf{12_1b}$: 120.1, 121.3, 123.8, 126.5, 126.9, 127.2,127.5, 127.7, 128.2, 128.8, 129.4, 129.8, 130.9, 134.5, 135.3, 136.1, 137.1, 138.8, 142.0, 144.5, 148.0; $\mathbf{12_2b}$: 121.8. 122.0, 122.5, 126.6, 126.7, 127.0, 127.2, 127.6, 127.9, 128.3, 128.9, 129.4, 129.9, 131.0, 134.5, 134.6, 135.2, 135.8, 136.3, 137.3, 139.6, 144.3, 146.5, 147.3.

10 1-Naphdata: *N*,*N*′,*N*″-tris(1-naphthyl)-1,3,5-trianilinobenzene, see: Y. Shirota, *SPIE*, **3148**, 186 (1990).

11 α-NPD: *N*,*N*′-bis(1-naphtyl)-*N*,*N*′-diphenylbenzidine, see: B. E. Koene, D. E. Loy, and M. E. Thompson, *Chem. Mater.*, **10**, 2235 (1998).

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