Synthesis of Thiazolinethione-5-Carbaldehydes by Vilsmeier-Haack formylation and transformation into Imines Chromophores

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Abstract: A new series of Shiff bases chromophores containing thiazole, rhodanine and dicyano moiety have been synthesized in four steps by functionalization of the corresponding Δ-4-thiazolinethione 1a-b via Vilsmeier-Haack reaction. The formylation of 1a has afforded to two aldehydes 3a and 3c. The orientation of this electrophilic substitution has been discussed. The structures of these newly compounds have been established on the basis of their analytical and spectral data.

Keywords: Thiazolinethione-5-Carbaldehydes, Synthesis, Vilsmeier-Haack formylation, transformation, Imines Chromophores.

Introduction

In the last three decades, heterocyclic chromophores are of wide interest because of their diverse potential applications in various fields as telecommunications, photovoltaic materials, information processors, optoelectronics and photonics.1

Synthetic approach to these chromophores mostly requires an intermediate such as aromatic aldehyde. Chromophores containing thiazole and benzothiazole units are versatile building blocks for the synthesis of donor-acceptor substituted n conjugated systems for several optical applications.2 Many researchers have demonstrated that heterocyclic chromophores containing thiazole ring exhibit higher hyperpolarizabilities (μβ) than their aryl analogues.3

Continuing of our efforts on the use of Δ-4-thiazolinethione 14 as starting material for the synthesis of new heterocycles with interesting chemical and physical properties, we have decided to synthesize novel Shiff bases chromophores by the functionalization of the corresponding Δ-4-thiazolinethione 1.


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In our previous work, we have studied the synthesis of several dyes rhodacyanines from a building block molecule, such as Δ-4-thiazolinethione 1. This compound has been easily prepared in reasonable amounts, ready for further applications. Indeed, we have used this compound as substrate for the functionalization at the 2 and 5-position of derivatives 1a-b.

The Vilsmeier-Haack reagent (chloromethylendiminium salt) which generated from an interaction of N,N-disubstituted formamides such as DMF with POCI₃ has attracted the attention of the synthetic organic chemists since its discovery in 1927. It has been extensively used for formylation of activated compounds and fully conjugated carboxylic system.

In this work we report the synthesis and the reactivity studies of thiazolcarboxaldehyde by Vilsmeier-Haack reaction from Δ-4-thiazolinethione 1a-b as starting materials. These resulting carboxaldehydes 3a-b have been used as syntheses for the production of new classes of Schiff bases chromophores 6a-d. The formylation of 1a has afforded two aldehydes 3a and 3c under Vilsmeier–Haack conditions.

As far as we know, the present study is the first one for the synthesis of formyl Δ-4-thiazolinethione 1 using Vilsmeier-Haack reagent. The formylation of thiazole and bisthiazolinethione derivatives has previously been prepared by the Sommelet réaction and metalation.

Experimental

Melting points were determined on a Kofler melting-point apparatus and are uncorrected. HNMR spectra were recorded on Bruker ARX 200 (200 MHz) and Bruker AC300P (300 MHz) spectrometers, and 13C NMR spectra were measured on a Bruker AC 300P (75 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. The mass spectra (HRMS) were measured on a Variant MAT 311 at an ionizing potential of 70 eV in the Centre de Mesures Physiques de l’Ouest (CRMPO, Rennes). Elemental analysis was performed at Centre de Mesures Physiques de l’Ouest (CRMPO, Rennes). The UV-Vis spectra were recorded on a UV-vis Spectrometer Pye Unicam at Tiaret University. All solvents and reagents were purchased from Acros Organics and Aldrich Chemic and used without further purification unless otherwise stated.

Starting Materials. The preparation of the compounds 1 was obtained according to the literature [4] from disulfide carbon, amine in aqueous ammonia, and chloroacetone by Hantzsch’s cyclization.

General procedure for the synthesis of products 3a and 3b: (Method A, Entry 3). The Δ-4-thiazolinethione 1 (50mmol, 1 eq) was dissolved in 60ml of 1, 2 dichloroethane with DMF (51.48mmol, 1.05eq, V = 4ml). The mixture was stirred for 10min at 0°C. The phosphorus oxychloride (51.48mmol, 1.05eq, V = 4.8ml) was added by slow addition. The reaction mixture was left at room temperature for 1h and heated at 80°C for 3h. The cooled reaction mixture was poured into ice cold water (30ml) and basified with NaOH solution (4M) to pH 9. The solid that separated was filtered, washed with water and crystallized from ethanol / water (80/20) to give compounds Δ-4-thiazolinethione -5-carbaldehydes 3.

Synthesis of 2, 3-Dihydro-3-((1E)-2-(3-dihydro-3,4-diméthyl-2- thioxothiazol-5-y1) vinyl)-4- méthyl-2-thioxothiazole-5-carbaldehyde 3c: Method B. Phosphorus oxychloride (50mmol, V= 4.7ml) was added dropwise at 0°C to DMF (775.2mmol, V = 60ml) and the reaction mixture was stirred for 20min. Thione 1a
(50mmol, m= 7.25g) dissolved in 20ml of DMF was added and maintained at room temperature for 1h. The mixture reaction was stirred at 80°C for 18h. After cooling, the mixture was poured into ice water and basified with NaOH (4M) and stirring for 4h. The solide was filtered, washed with ethanol /water (80/20).

Yield: 97%. Orange solid; mp > 260°C. $^1$HNMR (300MHZ, CDCl$_3$/TMS) $\delta$ppm = 9.55(s, 1H, CHO); 7.21-7.32(d, 1H, J = 15.2Hz); 6.32-6.37(d, 1H, J = 15.3Hz); 3.77(s, 3H, Me-Thiazol 1); 3.75(s, 3H, Me$_3$ thiazol 1); 2.9(s, 3H, Me$_2$ thiazol 2). $^{13}$CNMR (50MHZ, CDCl$_3$/TMS) $\delta$ppm = 109.09(Me=S). 1H NMR (80/20). 187.86(C=S); 182.87(dq, J=186Hz, CHO); 155.6(C$_2$thiazol 1); 154.01(C$_2$thiazol 2); 132.46(d, J = 161Hz,CH = C ) ; 120.6(d, J= 162Hz,CH=C). 116.81 (C$_2$thiazol); 113.01 (C$_2$thiazol); 35.27 (q, J = 142.2Hz, Me-Nthiazol 1); 13.58(q, J = 128.2Hz, Me-thiazol 1); 13.50(q, J = 18.1Hz, Me-thiazol 2). HRMS (EI) M. $^+$ for C$_5$H$_9$N$_2$S: calcd.: 237.9832; found: 237.9838.

General procedure for the preparation of Iminothiazolinethiones 4a-e. An equimolar mixture of 3a-b (5mmol) and primary aromatic amines (6 mmol) in absolute ethanol (20 mL) was heated under reflux for 1 h. The precipitate formed after cooling was filtered off, washed with cold ethanol, dried, and recrystallized from ethanol to give products 4.

3. 4-Diméthyl-5-((E)-(phénylimino) méthyl) thiazole-2(3H) -thione (4a). Yield: 82%. Yellow crystals; mp : 188°C. $^1$HNMR (200MHZ, CDCl$_3$/TMS) $\delta$ppm = 2.49(s, 3H, Me$_2$); 3.68(s, 3H, Me-N); 7.20-7.41(m, 5H); 8.37(s, 1H,CHN). $^{13}$CNMR (50MHZ, CDCl$_3$/TMS) $\delta$ppm = 13.98(Me$_2$thiazol) ; 34.25(Me-N) ; 115.13(C$_2$) ; 120.93 ; 126.50 ; 129.27 ; 143.10 ; (C$_a$) ; 147.58 (CH = N, J = 177Hz) ; 150.88 (C$_d$) ; 189.47(C=S). HRMS (EI) M. $^+$ for C$_5$H$_9$N$_2$S: calcd.: 248.0443; found: 248.0453.

5-((E)-(1-phényléthylimino) méthyl)-3,4-diméthylthiazole-2(3H)-thione (4b). Yield: 90% ; yellow solid ; mp : 196°C. $^1$HNMR (200MHZ, CDCl$_3$/TMS) $\delta$ppm =1.58(d, 3H, J= 6.63Hz); 2.4(s,3H,Me$_2$Thiazol); 3.57(s,3H,Me-N); 4.47(q,1H, J= 6.6Hz); 7.2- 7.40 ( m, 5H); 8.29(s,1H, CH= N). $^{13}$C NMR (50MHZ, CDCl$_3$/TMS) $\delta$ppm = 13.73 (Me$_2$thiazol) ; 25.02 (MeCPh) ; 34.21 (Me-N) ; 69.42 (CHMe) ; 116.52 ; 121.87 ; 126.2 ; 126.94 ; 128.2 (Car) ; 141.10 ; 144.61 (C$_d$) ; 147.88 (CH = N, J = 177Hz) ; 188.93(C=S). HRMS (EI) M. $^+$ for C$_8$H$_9$N$_2$S: calcd.: 276.0755; found: 276.0765.

5-((E)-(p-tolylimino)méthyl)-3,4-diméthylthiazole-2(3H)-thione (4c). Yield: 96%; yellow solid; mp: 146°C. $^1$HNMR (300MHZ, CDCl$_3$/TMS) $\delta$ppm = 2.29(s, 3H, Me-thiazol); 2.65(s,3H,Me-p-tolyl); 3.67(s, 3H, Me-N); 7.05-7.38 ( 2d, 4H); 8.55(s,1H,CH=N). $^{13}$C NMR (75MHZ, CDCl$_3$/TMS) $\delta$ppm=187.17(C=S); 152.09 (HC = S); 123.12Hz, Me$_2$thiazol); 21.17(q, J= 127.2Hz, Me-p tolyl); 35.35(q, J= 143.8Hz) ; 116.68 (C$_2$) ; 120.7 ; 125.87 ; 130.20 (Car) ; 142.95(C$_d$) ; 146.68(d, J = 177Hz, CH=N); 190.70(, C=S). HRMS (EI) M. $^+$ for C$_{13}$H$_{10}$N$_2$S: calcd.: 262.0598; found: 262.0613.

5- ((E)-(Benzylimino) méthyl)-3, 4-diméthylthiazole-2(3H)-thione (4d). Yield: 83%; yellow crystals; mp: 158°C. $^1$HNMR (300MHZ, DMSO) $\delta$ppm = 8.62(NMR (s, 1H, CHN)); 7.36-7.22 (m, 5H); 4.70 (s, 2H, CH$_2$Ph); 3.61(s, 3H, Me Nthiazol); 2.50(s, 3H, Me$_2$-thiazol). $^{13}$C NMR (50MHZ, DMSO) $\delta$ppm = 187.17(C=S); 152.09 (HC = N, J = 177Hz) ; 144.07 ; 139.29 ; 128.35 ; 128.27 ; 127.81 ; 126.79 ; 119.96; 63.22; 34.13 (MeN); 13.33 (Methiazol). HRMS (EI) M. $^+$ for C$_5$H$_9$N$_2$S: calcd.: 262.0598; found: 262.0651.

4- Méthyl-3-phényl-5-((E)-(phénylimino) methyl) thiazole-2(3H)-thione (4e). Yield: 86%; yellow crystals; mp: 190°C. $^1$HNMR (300MHZ, DMSO) $\delta$ppm = 2.15(s, 3H, Me$_2$ thiazol); 7.1-7.6(m, 10H); 8.4(s,1H, CH=N). $^{13}$C NMR (75MHZ, CDCl$_3$/TMS) $\delta$ppm = 14.63(MeC); 115.4(C$_2$); 122.70; 126.48; 128.15; 129.1; 129.92; 130.28; 137.26; 143.72 (Car); 147.75(C$_d$); 150.90(C = N); 191.21 (C = S). HRMS (EI) M. $^+$ for C$_{13}$H$_{10}$N$_2$S: calcd.: 310.0598; found: 310.0595.

General procedure for the preparation of Thiazolium Salts (5 a-c). A mixture of 4 (5 mmol), 15 mmol of CH$_3$I and 20 ml of CH$_3$CN is stirred at room temperature during 24 h. The resulting salt is filtered off and dried under vacuum.

3. 4-Diméthyl-2-(méthylthio)-5-[(phénylimino) méthyl]-1,3-thiazol-3-ioumiodore(5a). Yield: 85%; yellow crystals; mp: 198°C. $^1$HNMR (200MHZ, DMSO) $\delta$ppm = 2.52(s, 3H, Me$_2$); 2.6(s, 3H, Me-S); 3.88 (s, 3H, Me-N$^+$); 7.26-7.6 (m, 5H); 8.7 (s, 1H, CH = N). HRMS (EI) M. $^+$ for C$_{13}$H$_{10}$N$_2$S: calcd.: 263, 0676; found: 263, 0673.
3. 4-Diméthyl-2-(méthylthio)-5-[(1-phényléthyl) imino] méthyl]-1, 3-thiazol-3-iüm iodure (5 b). Yield: 80%; dark yellow crystals; mp : 186°C. 1HNMR (300HZ, D2O) δ ppm = 1.72 (s, 3H, Me-tolyl); 2.22 (s, 3H, Me); 2.40 (s, 3H, Me-S); 3.29 (s, 3H, Me-N); 6, 66-6.73 (2d, 4H); 9.39 (s,1H, CH = N).

3. 4-Diméthyl-5-[(4-méthylphényl) imino] méthyl]-2-(méthylthio)-1,3-thiazol-3-iüm iodure (5c). Yield: 95%; yellow crystals; mp: 212°C. 1HNMR (300HZ, CDCl3/TMS +TFA) δ ppm = 1.8(d, 3H, J = 6.9Hz, Methylene); 2.76 (s, Me-S); 2.90 (Me-N); 3.8 (s, MeCH); 5.9(m, 1H, CH, J= 6.8Hz); 7.7-7.5(m,).

General procedure for the synthesis of Schiff bases chromophores 6a-d. Activated methylene H2A (10mmol) was added to a solution of thiazolium salts 5 (10mmol) in acetone (30ml). After stirring 5min at room temperature, triethylamine was added (2ml). The reaction mixture immediately turns red. The magnetic stirring is maintained at room temperature overnight. The solid obtained is filtered and washed with acetone.

(5E)-3-Méthyl-5-(3, 4-diméthyl-5-[(phényléthyl) imino] thiazol -2(3H)-ylidène)-2-thioxo-thiazido lindin-4-one (6a). Yield: 87%; red solid; mp : > 260°C. UV-Vis (MeOH) λ max=420nm. 1HNMR (300HZ, CDCl3/TMS +TFA) δ ppm = 1.27(d,3H,J= 7.36Hz); 2.4(s,3H, Me); 3.3 (s, 3H, Me-Nhrhod); 3.8 (s, 3H, Me-thiazol); 4.9 (m,1H, J = 6.8Hz); 7.15-7.3 (m,5H); 8.4 (s, 1H, CH = N). 13CNMR (75MHZ,CDCl3/TMS+ TFA) δ ppm = 13.9(s,3H,J= 132.4Hz, Me3 thiazol);20.30(qd, J = 130Hz, MeCH);31.63 (q, J = 143Hz, Me-Nrhod);35.93 (q, J = 143.7Hz, Me-Nthiazol); 64.2 (dm, J= 143.8, CHMe);93.05(C5rhod); 109.45 (C5thiazol); 112.74; 116.52; 126.66; 129.49; 129.66; 130.08; 136.84; 164.25 (d, J= 197Hz, CH=N); 167.23(C=O) ; 188.22(C=S)150.39(C2);154.2(C2thiaz); 167.23(C=O); 188.22(C=S). HRMS (EI): M+ for C28H23N7O3S4 calcd: 539.0694; found: 539.0694. QUALITATIVE ANAL. calcd for C28H23N7O3S4: C, 45.25; H, 3.43; N, 15.47; S, 19.53; Found: C, 45.19; H, 3.34; N, 15.33; S, 19.24.

(5E)-[3,4-Diméthyl-5-[(1-phényléthyl)imino]méthyl]-1,3-thiazol-2(3H)-ylidène]-3-méthyl-2-thioxo-1,3-thiazolidin-4-one (6b). Yield: 79%; dark green solid; mp : > 260°C. UV-Vis (MeOH) λ max=489nm. 1HNMR (300HZ, CDCl3/TMS +TFA) δ ppm = 2.4 (s, 3H); 2.72 (s, 3H, Me); 3.5(s, 3H, Me-Nrhod); 3.92 (s, 3H, Me-Nthiazol);7.24-7.40 (m, 4H); 8.83 (s,1H, CH = N). 13CNMR (75MHZ,CDCl3/TMS) δ ppm = 13.95 (q, J = 132.62Hz, Me-thiazol);21.15 (q, J = 127Hz, Me-tolyl);31.7 (q, 143.3Hz, Me-Nrhod); 36.3 (q, J = 143.7Hz, Me-Nthiazol);94.58 (C=O); 109.53 (C(5thiazol);119.97 ;134.8(C);150.58 (C(5thiazol); 163.72(d, J = 190Hz, CH = N);168.3 (C=O);189.34 (C=S). HRMS (EI): M+ for C28H23N7O3S4 calcd: 539.0534; found: 537.0539. Anal. Calcd for C28H23N7O3S4: C, 54.37; H, 4.56; N, 11.19; S, 25.62. Found: C, 54.39; H, 4.62; N, 11.25; S, 25.69.

2-(3,4-Diméthyl-5-[(phénylimino)méthyl]thiazol-2(3H)-ylidène)malononitrile(6d). Yield: 82%; dark yellow solid; mp : > 260°C. UV-Vis (MeOH) λ max= 418nm. 1HNMR (300HZ, CDCl3/TMS +TFA) δ ppm = 2.6(s, 3H, Me); 2.9 (s, 3H, NMMe); 7.44-7.6 (m, 5H); 9.01(s, 1H, CH=N). HRMS (EI): M+ for C13H12N4O calcd.: 308.0782; found: 308.0792. Anal. Calcd for C13H12N4S: C, 64.26; H, 4.31; N, 19.98; S, 11.44. Found: C, 64.32; H, 4.38; N, 11.25; S, 19.26.

Results and Discussion

The formylation reaction of 4-thiozalinethione 1a using V-H reagent with different amounts of POCl3/DMF and at different reaction temperatures has investigated in order to optimize the reaction conditions. The optimization of the amounts of phosphorus oxychloride and DMF is summarized in Table 1. It has been found that the best yield of the corresponding formyl 3a has been obtained at 80°C for 3 hours with 1equiv of POCl3/DMF in 1,2 dichloroethane (Table1, Entry 3). Without chlorinated solvents such as 1, 2 dichlorehthane, has improved yield of aldehyde 3a at 60°C has led to aldehyde 3a in 62% yields (Entry 4). At room temperature, 3a has not been obtained (Entry5).
Therefore, the same V.H formylation of 1a with DMF/POCl₃ at 80°C for 18h has produced a mixture of formyl derivatives. The mixture was purified by column chromatography on silica gel (CH₂Cl₂) to give 3a (60%) and 3c (15%) (Table 1, Entry 6).

Table1. Selected optimization of Vilsmeier-Haack formylation Δ-4-thiazolinethione 1a (Method A)

<table>
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<tr>
<th>Entry</th>
<th>POCl₃(equiv)</th>
<th>DMF(equiv)</th>
<th>DCEb(ml)</th>
<th>T°C</th>
<th>Time(h)</th>
<th>Yield(%) ³ 3a/3c</th>
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<tr>
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<td>18</td>
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³Isolated yield
b 1, 2 dichloroethane

We adopted the experimental protocol according to Entry 3 for the synthesis of 3a and 3b.

The formylation reaction of Δ-4-thiazolinethione 1a-b in dichloroethane (60ml) with DMF/POCl₃(1eq) at 0°C; followed by stirring reaction mixture at 80°C for 3h and neutralization with NaOH (4M) has afforded to 2,3-dihydro-3,4-dimethyl-2-methylenethiazole-5-carbaldehyde 3a in 75% yield and 2,3-dihydro-4-methyl-2-methylene-3-phenylthiazole-5-carbaldehyde 3b in 46% yield (Scheme1).

Scheme 1

The structure of the compound 3c was elucidated from its spectral data.

The ¹H NMR spectrum of 3c showed the presence of two doublet at 6.34 and 7.32ppm corresponding to CH=CH, with coupling constants of J= 15.34Hz, characteristic of E configuration. The proton signal appearing around 9.55ppm confirmed the presence of group formyl CHO at C₅ position of the Δ-4-thiazolinethione Δ-4-thiazolinethione 1a.
This unexpected result (Table 1, Entry 6) leads us to investigate this formylation using a different procedure from the first, by the direct preparation of the 3c as exclusive product from 1a under VH conditions (Method B): The POCl3/DMF (1equiv) /15.5eq) is stirred at 0 °C, a thione solution 1a in DMF (20ml) is added to the reactant in small fractions VH. The mixture is brought to réactionnel 1h at rt, then heated to 80 ° C for 18 h. The aldehyde 3c is obtained quantitatively (97%) (Scheme1).

These results show that in the case of Vilsmeier formylation of thiazoline thione 1a, the reaction occurs in the most activated position 3 and 5. The results indicate that the 5-position is still favoured compared to the 3-position. The structures were confirmed by 1H, 13C NMR and HRMS. The formyl group has been introduced at carbon C5 as proposed in the following mechanisms (Scheme 2).

Scheme 2
Initially, chloromethyleniminium salt interacts with the thione 1a to give in situ the corresponding monomethyliminium salt 2a which further reacts with another chloromethyleniminium salt to afford after neutralization with NaOH the formyl 3c (Scheme 3).

On the other hand, a large number of heterocyclic Schiff bases containing thiazole moiety have been reported to possess several biological activities. Some of the Schiff bases were used as chromophores in NLO applications. The synthetic strategy adopted to obtain the target compounds is depicted in the scheme 4.
Condensation of thiazolinethione-5-carboxaldehyde 3a-b with primary aromatic amines in refluxing ethanol gave Schiff bases 4a-e in good yields (82-96%. Table 2). These Schiff bases are engaged in an alkylation reaction in the presence of an excess of iodomethane at room temperature for 2h. Salts 5a-c (table 2) obtained were isolated by filtration and purified by simply washing with acetone. The condensation reaction of the salt 5 with activated methylenes in the presence of triethylamine in acetone at room temperature leads to imines chromophores 6 with good yields (70-87%, Table3). All compounds were unambiguous confirmed by their analytical and spectral data.

Table 2. Physico-chemical data of Schiff bases 4a-e and thiazoliums salts 5a-d

<table>
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<th>Composés</th>
<th>R₁</th>
<th>R₂</th>
<th>Yield %</th>
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<td>4a</td>
<td>Me</td>
<td>Ph</td>
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<tr>
<td>4b</td>
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<td>Ph</td>
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Table 3. Physico-chemical data of 6a-h

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<th>Yield (%)</th>
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<td>Me</td>
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Conclusion

In summary, formyl thiazolinethiones 3 have been synthesized through the V-H reaction starting from easily available precursor as Δ-4-thiazolinethione 1 which is obtained by Hantzsch’s reaction. Four synthetic routes have been widely used for the preparation of Schiff bases chromophores 6a-d; Formylation of 1a-b, condensation of an aldehyde 3a-b with primary aromatic amines, followed by alkylation with an excess iodide methane and finally, condensation with activated methylenes. The formation of formyl 3c was described and a mechanism was proposed. Formyl derivative 3c compound containing two thiazoles moiety in a single molecular framework, could be used as important building blocks in the synthesis of various heterocycles which often show high biological activities and promising applications in optoelectronics.

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Références


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