



HAL
open science

Synthesis via direct (hetero)arylation polymerization, electrochemical and optical properties of poly (3,4-disubstituted)thiophenes

Jérémie Grolleau, Stéphanie Legoupy, Pierre Frère, Frédéric Gohier

► To cite this version:

Jérémie Grolleau, Stéphanie Legoupy, Pierre Frère, Frédéric Gohier. Synthesis via direct (hetero)arylation polymerization, electrochemical and optical properties of poly (3,4-disubstituted)thiophenes. *Polymer*, 2019, 182, pp.121811. 10.1016/j.polymer.2019.121811 . hal-02307410

HAL Id: hal-02307410

<https://hal.science/hal-02307410v1>

Submitted on 21 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Synthesis via direct (hetero)arylation polymerization, electrochemical and optical properties of poly (3,4-disubstituted)thiophenes

Jérémie Grolleau, Stéphanie Legoupy, Pierre Frère* and Frédéric Gohier*

MOLTECH-Anjou, UMR 6200, CNRS, UNIV Angers, SFR MATRIX, 2 bd Lavoisier, 49045 ANGERS Cedex, France

email : pierre.frere@univ-angers.fr; frederic.gohier@univ-angers.fr

Abstract

Some poly (3,4-disubstituted)thiophenes bearing both cyano and alkoxy or thioalkoxy groups have been synthesized by direct (hetero)arylation polymerization (DHAP) of 2-iodo-3,4-disubstituted thiophenes. The electron donor and acceptor properties of substituents in positions 3 and 4 allow to adjust the HOMO and LUMO levels. On the other hand, in order to avoid the polymer solubility problems, long branched or unbranched alkyl chains have also been introduced. Thus polymers with alkoxy groups have led to complete absorption in the wavelength range of the visible spectrum whereas in the presence of thioalkoxy groups, the absorption of the visible spectrum is only partial. Theoretical calculations have shown that sulphur creates torsions leading to a non-planar polymer chain.

Key words: polythiophenes, direct heteroarylation polymerization, electronic properties

1-Introduction

Thiophene is a **building block** that will be found in many materials for optoelectronic applications. **Polythiophenes are** easily obtained, for example by Grignard Metathesis Polymerizations (GRIM), ^[1] **Pd-catalyzed cross-coupling polycondensation**^[2] or more recently by direct arylation polymerization ^[3] which simply involves a C-H bond and a C-halogen bond so that the reaction can take place. There are a large number of papers describing polymers and copolymers based on thiophene using this methodology and a recent review by Pr Leclerc includes a number of examples.^[4] P3HT, which has long remained the reference polymer as donor in organic photovoltaic cells ^[5], has been synthesized from bromo derivatives using Pd/NHC precursors, ligand and pivalic acid. ^[6] It can be synthesized in a simpler way, using Pd/C in phosphine free conditions. ^[7] **Study on such type of polymers seems** to be a way to explore to improve its properties for photovoltaic applications.

The energy levels of the HOMO and LUMO orbitals and therefore the bandwidth of the conjugated polymers can be controlled by the insertion of electron donor (D) and electron acceptor (A) **units based on 3 and 4-substituted thiophenes**. The electronic properties of **conjugated polymers** are highly dependent on the distribution of groups D and A along the conjugated skeleton. Introduction of cyano group **into** P3HT ^[8] affects the optoelectronic properties. **The conjugation length is reduced which leads to an increase in the band gap**. If an alkoxy chain replaces the hexyl chain in P3HT, **the absorbance window is larger and the band gap is lowered**. ^[9] Polymers carrying a cyanothiophene unit alternating or randomly with an alkylthiophene ^[10] as well as alkoxythiophene unit, ^[11] **have already been reported so far**. **These materials result suitable optoelectronic properties in photovoltaic applications**. **Recently**, we have synthesized thiophenes with an alkoxy group and cyano group.^[12] We have shown that thiophene containing cyano and hexyloxy groups has electrochemical properties comparable to thiophene containing only the cyano group. **However**, optical properties were different. In this paper, we present the results of this same unit but within homopolymers. We also studied the effect of S in thioalkoxy chain instead of alkoxy chain on the properties of polymers.

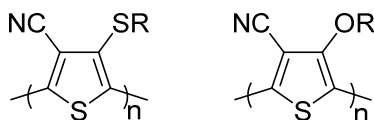


Figure 1

2-Experimental

2.1. Materials

NMR spectra were recorded on a Bruker Avance 300 (^1H : 300.1 MHz, ^{13}C : 75.7 MHz, T = 300 K). Spectra were referenced against the internal NMR-solvent standard. Chemical shifts were expressed in parts per million (ppm) and were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants J were given in Hz. Mass spectra were recorded under EI mode on a VG-Autospec mass spectrometer. The main peaks are described according to m/z . The peak corresponding to molecular mass is expressed as (M^+). Analytical grade solvents were used. Molecular weight analyses were performed on a Viscotek apparatus, composed of a GPC Max (comprising a degasser, a pump and an autosampler) with RI refractive index detector using a calibration with PS (sample from 1500g/mol to 1 500 000 g/mol with IP close to 1). THF was used as the eluent with a flow rate of 1.0 ml.min $^{-1}$ at 30 °C. UV-Vis absorption spectra were recorded at room temperature on a Perkin Elmer Lambda 950 spectrometer and a PTI spectrofluorimeter mod. Quanta Master 1 coupled with a thermostat, using a Xenon lamp (70 W) as source and slits of 1 nm in a conventional quartz cell (light pass 10 mm). TGA analyses were performed with TA Instruments Q500. DSC analyses were performed with TA Instruments Q20. Cyclic voltammetry was performed using a Biologic SP-150 potentiostat with positive feedback compensation in dichloromethane solutions purchased from Carlo Erba (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.1 M as supporting electrolyte) was purchased from Sigma-Aldrich. Experiments were carried out in a one-compartment cell equipped with platinum working microelectrode ($\varnothing = 2$ mm) and a platinum wire counter electrode. An Ag/AgNO $_3$ (0.01 M in CH $_3$ CN) electrode was used as reference and checked against the ferrocene/ferricinium couple (Fc $^+$ /Fc) before and after each experiment. Theoretical calculations were done using the density functional theory with the Gaussian 09 program. The geometric optimization is based on the B3LYP hybrid functional with the 6-31G base (d, p).

2.2. Synthesis

The compounds **1**, ^[13] **2a** and **3a** ^[14] were synthesized from experimental data in the literature.

2.2.1. Synthesis of 4-(octadecyloxy)-2,5-dihydrothiophene-3-carbonitrile **2b**

To a solution of 4-oxotetrahydrothiophene-3-carbonitrile (1.02 g, 8.05 mmol) in dimethylformamide (10 mL), cesium carbonate (3.47 g, 10.65 mmol, 1.3 eq) and octadecyl methanesulfonate (3.56 g, 10.21 mmol, 1.3 eq) were added. The mixture was irradiated in CEM microwave open vessel (P:200 W, T:130°C) for 5 min. The mixture was poured into water, neutralized with diluted HCl (2M) and extracted with EtOAc (2 times). The organic layer was washed with saturated solution of NaCl, then water and dried over MgSO $_4$. The solvent was evaporated and the crude was purified through silica gel (petroleum ether/methylene chloride 1/1) to give a white solid (1.85g, 61%). mp 48-50°C. ^1H NMR (300 MHz, CDCl $_3$, ppm): δ 4.31 (t, 2H, J=6.6 Hz), 3.76 (s, 4H), 1.77-1.65 (m, 2H), 1.44-1.18 (m, 30H), 0.92-0.84 (m, 3H). ^{13}C NMR (77.16 MHz, CDCl $_3$, ppm): δ 169.1, 115.9, 80.7, 72.5, 36.2, 34.3, 32.0, 29.8, 29.7, 29.6, 29.5, 29.3, 25.7, 22.8, 14.2. HRMS (EI) calcd for C $_{23}$ H $_{41}$ NOS [M^+]: 379.2909, found: 379.2905.

2.2.2. Synthesis of 4-(decyloxy)-2,5-dihydrothiophene-3-carbonitrile **2c**

To a solution of 4-oxotetrahydrothiophene-3-carbonitrile (1.01 g, 7.94 mmol) in dimethylformamide (10 mL), cesium carbonate (3.1 g, 9.51 mmol, 1.2 eq) and 3,7-dimethyloctyl methanesulfonate (2.42 g, 10.24 mmol, 1.3 eq) were added. The mixture was irradiated in CEM microwave open vessel (P: 200 W, T:130°C) for 5 min. The mixture was poured into water, neutralized with diluted HCl (2M) and extracted with EtOAc (2 times). The organic layer was washed with saturated solution of NaCl, then water and dried over MgSO₄. The solvent was evaporated and the crude was purified through silica gel (petroleum ether/methylene chloride 1/1) to give a plate yellow oil (1.06g, 50%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 4.42-4.27 (m, 2H), 3.76 (s, 4H), 1.81-1.68 (m, 1H), 1.65-1.45 (m, 3H), 1.34-1.09 (m, 6H), 0.91 (d, 3H, J=6.4 Hz), 0.86 (d, 6H, J=6.6 Hz). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 169.1, 115.9, 80.7, 70.9, 39.3, 37.2, 36.4, 36.3, 34.3, 29.6, 28.1, 24.7, 22.8, 22.7, 19.6. HRMS (EI) calcd for C₁₅H₂₅NOS [M⁺]: 267.1657, found: 267.1660.

3.3.3 4-(octadecyloxy)thiophene-3-carbonitrile **3b**

To a solution of 4-(octadecyloxy)-2,5-dihydrothiophene-3-carbonitrile (1g, 2.63 mmol) in methylene chloride (30 mL) was stirred at 50°C then a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (720 mg, 3.17 mmol, 1.2 eq) in THF (8 mL) was slowly added dropwise, and the mixture was stirred overnight at 50°C. After addition of water, the mixture was extracted with methylene chloride. The organic layer was dried over MgSO₄ and the solvent was removed under vacuum. The resulting crude product was purified over silica gel to give a white solid (655 mg, 66%). mp 75-77°C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.76 (d, 1H, J=3.3 Hz), 6.26 (d, 1H, J=3.3 Hz), 3.99 (t, 2H, J=6.5 Hz), 1.87-1.76 (m, 2H), 1.50-1.21 (m, 30H), 0.90-0.85 (m, 3H). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 157.7, 134.1, 113.5, 104.2, 98.0, 71.4, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.0, 26.0, 22.8, 14.2. HRMS (EI) calcd for C₂₃H₃₉NOS [M⁺]: 377.2752, found: 377.2747.

3.3.4 4-(decyloxy)thiophene-3-carbonitrile **3c**

To a solution of 4-(decyloxy)-2,5-dihydrothiophene-3-carbonitrile (800 mg, 3.01 mmol) in methylene chloride (30 mL) was stirred at 50°C then a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (815 mg, 3.59 mmol, 1.2 eq) in THF (8 mL) was slowly added dropwise, and the mixture was stirred overnight at 50°C. After addition of water, the mixture was extracted with methylene chloride. The organic layer was dried over MgSO₄ and the solvent was removed under vacuum. The resulting crude product was purified over silica gel to give a colorless oil (718 mg, 90%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.76 (d, 1H, J=3.3 Hz), 6.27 (d, 1H, 3.3 Hz), 4.07-4.00 (m, 2H), 1.92-1.80 (m, 1H), 1.71-1.46 (m, 3H), 1.36-1.10 (m, 6H), 0.94 (d, 3H, J=6.4 Hz), 0.87 (d, 6H, J=6.6 Hz). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 157.7, 134.2, 113.5, 104.2, 98.0, 69.8, 39.3, 37.3, 35.9, 29.9, 28.1, 24.7, 22.8, 22.7, 19.7. HRMS (EI) calcd for C₁₅H₂₃NOS [M⁺]: 265.1500, found: 265.1494.

3.3.5 4-(hexylthio)thiophene-3-carbonitrile **6a**

A solution of 4-bromothiophene-3-carbonitrile (465 mg, 2.47 mmol), tributyl(hexylthio)stannane (2.05 g, 5.03 mmol, 2 eq), and Pd(PPh₃)₄ (850 mg, 0.74 mmol, 30% mol) in dry toluene (25 mL) was heated at 120°C for 12 h. The organic layer was diluted with EtOAc and washed with an aqueous solution of NaHCO₃, then water, dried over MgSO₄ and the solvent was removed under vacuum. The crude was purified over silica gel (methylene chloride/petroleum ether 6/4) to give a yellow oil (507 mg, 91%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.95 (d, 1H, J=3.2 Hz), 7.22 (d, 1H, J=3.2 Hz), 2.91 (t, 2H, J=7.4 Hz), 1.67-1.57 (m, 2H), 1.46-1.36 (m, 2H), 1.31-1.25 (m, 4H), 0.88 (t, 3H, 6.8 Hz). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 136.5, 135.1, 125.7, 114.6, 114.2, 35.5, 31.4, 29.6, 28.4, 22.6, 14.1. HRMS (CI) calcd for C₁₁H₁₅NS₂ [M⁺]: 225.0646, found: 225.0647.

3.3.6 4-(octadecylthio)thiophene-3-carbonitrile **6b**

A solution of 4-bromothiophene-3-carbonitrile (502 mg, 2.67 mmol), tributyl(hexylthio)stannane (3.2 g, 5.56 mmol, 2 eq), and Pd(PPh₃)₄ (932 mg, 0.81 mmol, 30% mol) in dry toluene (15 mL) was heated at 120°C for 12 h. The organic layer was diluted with EtOAc and washed with an aqueous solution of NaHCO₃, then water, dried over MgSO₄ and the solvent was removed under vacuum. The crude was purified over silica gel (methylene chloride/petroleum ether 6/4) to give a plate yellow solid (771 mg, 73%). mp 57-59°C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.95 (d, 1H, J=3.2Hz), 7.22 (d, 1H, J=3.2 Hz), 2.91 (t, 2H, J=7.4 Hz), 1.68-1.55 (m, 2H), 1.46-

1.19 (m, 30H), 0.91-0.83 (m, 3H). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 136.4, 135.0, 125.5, 114.5, 114.1, 35.4, 32.0, 29.8, 29.7, 29.6, 29.5, 29.2, 28.7, 22.8, 14.2. HRMS (EI) calcd for C₂₃H₃₉NS₂ [M⁺]: 393.2524, found: 393.2517.

3.3.7 4-(hexyloxy)-5-iodothiophene-3-carbonitrile **4a**

4-(hexyloxy)thiophene-3-carbonitrile (202 mg, 0.97 mmol) was dissolved in EtOH (8 mL) at 50°C. Then, NIS (452 mg, 2 mmol, 2.1 eq) was added followed by PTSA (18mg, 0.1 mmol, 10%mol). The mixture was stirred 10 min, then saturated Na₂S₂O₃ (2 mL) was added. The mixture was diluted with EtOAc. After organic layer was washed with 1M Na₂CO₃ solution, dried over MgSO₄, filtered, and evaporated to give a yellow oil (320 mg, 98%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.96 (s, 1H), 4.20 (t, 2H, J=6.5 Hz), 1.85-1.75 (m, 2H), 1.57-1.46 (m, 2H), 1.39-1.31 (m, 4H), 0.91 (t, 3H, J=7.0 Hz). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 159.2, 139.4, 112.8, 105.9, 75.4, 62.2, 31.6, 30.0, 25.6, 22.7, 14.2. HRMS (EI) calcd for C₁₁H₁₄INOS [M⁺]: 334.9841, found: 334.9831.

3.3.7 5-iodo-4-(octadecyloxy)thiophene-3-carbonitrile **4b**

4-(octadecyloxy)thiophene-3-carbonitrile (200.5 mg, 0.54 mmol) was dissolved in EtOH (4 mL) at 50°C. Then, NIS (252 mg, 1.12 mmol, 2.1 eq) was added followed by PTSA (11mg, 0.06 mmol, 10%mol). The mixture was stirred 10 min, then saturated Na₂S₂O₃ (2 mL) was added. The mixture was diluted with EtOAc. After organic layer was washed with 1M Na₂CO₃ solution, dried over MgSO₄, filtered, and evaporated to give a yellow oil (270 mg, 99%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.96 (s, 1H), 4.20 (t, 2H, J=6.5 Hz), 1.85-1.75 (m, 2H), 1.55-1.20 (m, 30H), 0.91-0.85 (m, 3H). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 159.1, 139.3, 112.7, 105.8, 75.4, 62.2, 32.0, 30.0, 29.8, 29.7, 29.5, 29.4, 25.9, 22.8, 14.2. HRMS (EI) calcd for C₂₃H₃₈INOS [M⁺]: 503.1719, found: 503.1720.

3.3.8 4-(decyloxy)-5-iodothiophene-3-carbonitrile **4c**

4-(decyloxy)thiophene-3-carbonitrile (311 mg, 1.17 mmol) was dissolved in EtOH (6 mL) at 50°C. Then, NIS (514 mg, 2.28 mmol, 2 eq) was added followed by PTSA (20 mg, 0.12 mmol, 10%mol). The mixture was stirred 10 min, then saturated Na₂S₂O₃ (3 mL) was added. The mixture was diluted with EtOAc. After organic layer was washed with 1M Na₂CO₃ solution, dried over MgSO₄, filtered, and evaporated to give a yellow oil (411 mg, 90%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.96 (s, 1H), 4.31-4.18 (m, 2H), 1.92-1.80 (m, 1H), 1.79-1.67 (m, 1H), 1.66-1.46 (m, 2H), 1.38-1.11 (m, 6H), 0.96 (d, 3H, J=6.5 Hz), 0.87 (d, 6H, J=6.6 Hz). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 159.2, 139.4, 112.7, 105.8, 73.8, 62.2, 39.4, 37.3, 37.1, 29.6, 28.1, 24.8, 22.8, 22.7, 19.7. HRMS (EI) calcd for C₁₅H₂₂INOS [M⁺]: 391.0467, found: 391.0457.

3.3.9 4-(hexylthio)-5-iodothiophene-3-carbonitrile **7a**

4-(hexylthio)thiophene-3-carbonitrile (100.5 mg, 0.45 mmol) was dissolved in EtOH (4 mL) at 50°C. Then, NIS (111 mg, 0.49 mmol, 1.1 eq) was added followed by PTSA (8mg, 0.048 mmol, 10%mol). The mixture was stirred 10 min, then saturated Na₂S₂O₃ (2 mL) was added. The mixture was diluted with EtOAc. After organic layer was washed with 1M Na₂CO₃ solution, dried over MgSO₄, filtered and evaporated to give a yellow oil (148 mg, 94%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.07 (s, 1H), 2.89 (t, 2H, J=7.2 Hz), 1.6-1.49 (m, 2H), 1.47-1.37 (m, 2H), 1.32-1.23 (m, 4H), 0.87 (t, 3H, J=6.9 Hz). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 141.0, 139.9, 116.0, 113.7, 88.3, 36.4, 31.4, 29.7, 28.3, 22.6, 14.2. HRMS (EI) calcd for C₁₁H₁₄INS₂ [M⁺]: 350.9612, found: 350.9615

3.3.10 5-iodo-4-(octadecylthio)thiophene-3-carbonitrile **7b**

4-(octadecylthio)thiophene-3-carbonitrile (301 mg, 0.76 mmol) was dissolved in EtOH (6 mL) at 50°C. Then, NIS (344 mg, 1.53 mmol, 2 eq) was added followed by PTSA (18 mg, 0.1 mmol, 10%mol). The mixture was stirred 10 min, then saturated Na₂S₂O₃ (3 mL) was added. The mixture was diluted with EtOAc. After organic layer was washed with 1M Na₂CO₃ solution, dried over MgSO₄, filtered, and evaporated to give a white solid

(358 mg, 91%). mp: 81-83°C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.07 (s, 1H), 2.88 (t, 2H, J=7.2 Hz), 1.61-1.49 (m, 2H), 1.45-1.21 (m, 30H), 0.91-0.84 (m, 3H). ¹³C NMR (77.16 MHz, CDCl₃, ppm): δ 140.9, 139.9, 116.0, 113.6, 88.2, 36.3, 32.0, 29.8, 29.7, 29.6, 29.5, 29.2, 28.6, 22.8, 14.2. HRMS (EI) calcd for C₂₃H₃₈INS₂ [M⁺]: 519.1490, found: 519.1475.

3.3.11 General procedure for direct arylation polymerization:

A mixture of 4-(alkyl)-5-iodothiophene-3-carbonitrile (200 mg), potassium carbonate (3 eq) and palladium acetate (10% mol) was stirred in *N,N*-dimethylformamide (6 mL) for 40 h at 80°C under an argon atmosphere. An aqueous solution was added, and the precipitate was separated by filtration and washed with distilled water and methanol. The precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 4 h with methanol then 20 h with hexane. The polymer was finally collected from chloroform, and the resulting solution was then concentrated by evaporation to give the desired polymers.

Poly-4-(octadecyloxy)thiophene-3-carbonitrile **Poly 4b**

Dark powder, 63 %. SEC: M_n (KDa)= 7.6, M_w (KDa)=16.1, PDI=2.1

Poly-4-(decyloxy)thiophene-3-carbonitrile **Poly 4c**

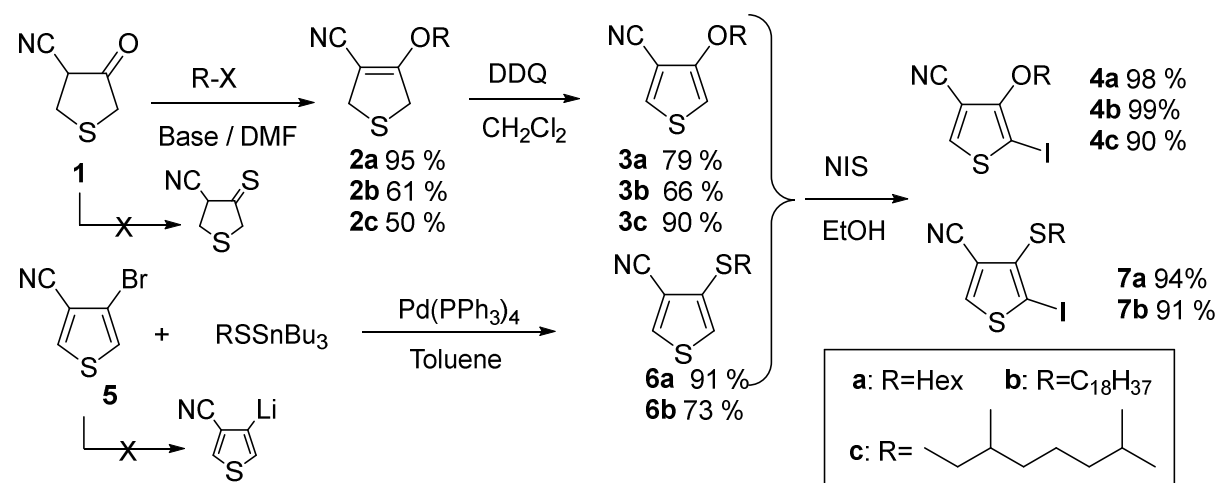
Dark powder, 69 %. SEC: M_n (KDa)= 7.5, M_w (KDa)=21.0, PDI=2.8

Poly-4-(octadecylthio)thiophene-3-carbonitrile **Poly 7b**

Dark powder, 36 %. SEC: M_n (KDa)= 1.8, M_w (KDa)=5.8, PDI=3.2

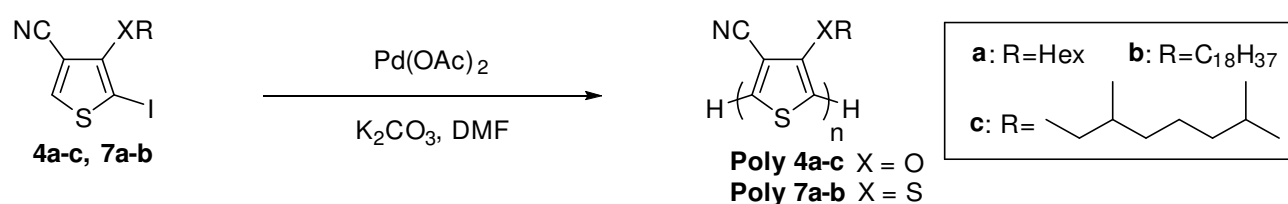
3. Results and discussion

Access to the various monomers was achieved by two synthesis methods. The first allows synthesis of compounds **4** from compound **1** and the second allows the introduction of thioalkoxy chain from brominated derivative **5** to lead to derivatives **7**. Compound **1** obtained by condensation of acrylonitrile with ethyl thioglycolate ester leads to derivatives **2** by alkylation of enolate following by aromatization to obtain the thiophene **3**. Attempts to obtain thioketone from ketone **1** via Lawesson's reagent failed. Thioalkyl chains were therefore introduced by Stille cross-coupling since the bromine-lithium exchange does not allow the functionalization of position 3 due to lithium dance in position 2. The iodination is then carried out with excellent yields without any purification according to a protocol we have reported.^[15]



Scheme 1: Syntheses of thiophene monomers

The polymer synthesis was carried out according to a direct arylation polymerization.^[3b] Simple conditions were used based on the work of Lemaire et al. ^[16] The polymerization of the various monomers was carried out at 80°C in DMF with Pd(OAc)₂ as catalyst and K₂CO₃. In Lemaire's procedure, they used Bu₄NBr, however, in our case, the results are identical with or without this co-reagent. The addition of the catalyst in the medium causes a colour change from red to black blue. The resultant polymers are purified by Soxhlet extraction with different solvents to remove unpolymerized organic compounds. Polymer **4a** with the hexyl chain could not be analyzed due to its insolubility in common organic solvent and monomer **7a** could not polymerize. When a C18 linear chain is present, the polymers are more soluble, however the yield for the thioalkyl polymer (**Poly 7b**) is modest (36%). Sulphur containing species are known to have poisoning effects on metal catalyst, which has been confirmed by direct arylation tests with monomer **6a**. Indeed, **6a** in presence of bromobenzene, catalyst, ligand and base could not be functionalized; such result explains the impossibility to obtain **poly 7a**. Polymerizations with alkoxy were obtained with good yields (63 and 69% for **4b** and **4c**), the polymers being quite soluble.



Scheme 2: Polymerization of thiophene monomers

Molecular weights were measured by SEC and indicate that polymers were obtained with quite short chains (around 9000 g/mol for **poly 4b** and **poly 4c**) and with a high polydispersity. Very short chains for the thioalkyl derivative (2000 g/mol) were detected in SEC confirming the difficulty to polymerize the thioalkyl derivative. The degradation temperatures of the various polymers were also determined by TGA and proved satisfactory for applications such as solar energy as materials begin to degrade around 280°C for **poly 4** (see SI). DSC analyses were also done on the different materials and showed transition glass between 50 °C and 70°C (see SI) for **poly 4a** and **poly 7b**.

Optical properties of the polymers were analyzed by UV-Visible spectroscopy in solution in chloroform (Figure 2a) and in thin film deposited on glass by spin-coating (Figure 2b).

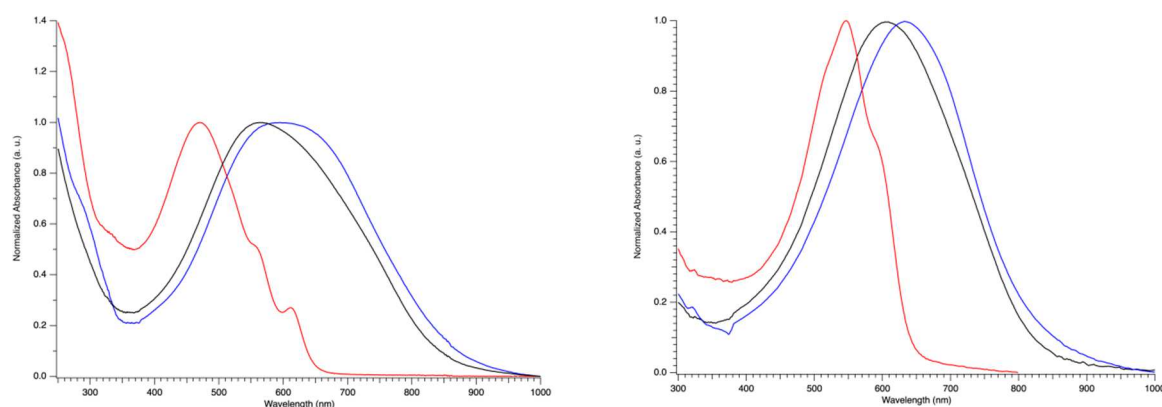


Figure 2: a) UV-Visible spectra of **poly 4b** (black), **poly 4c** (blue) and **poly 7b** (red) in CHCl₃. b) UV-Visible spectra of films on glass of **poly 4b** (black), **poly 4c** (blue) and **poly 7b** (red).

The **poly 4b** and **poly 4c** polymers have a wide absorption band centered at 565 and 605 nm respectively, covering the spectrum from 400 to 800 nm. The absorption band of the **poly 7b** at 472

nm has several shoulders that may be due to a mixture of oligomers, in accordance with the broad polydispersity observed in SEC. On film, displacements of about 40, 30 and 75 nm are observed for **poly 4a**, **poly 4b** and **poly 7b** respectively. The observed bathochromic displacement results from a reorganization of the polymer chains in the solid state and its skeleton (stacking). For **poly 7b**, this effect is more important, meaning an increase of conjugation in solid state. Our attention has been drawn to the hypsochromic displacement of **poly 7b** in comparison with **poly 4**. This can be explained by the larger sulfur atom creating an S---S repulsion then causing a conjugation breakdown.^[17] In contrast, in **poly 4b** and **poly 4c**, S---O interactions are favourable and increase electron delocalization.^[18] In order to check the influence of donor and acceptor groups on the same thiophene motif on electronic properties, theoretical calculations using the density functional theory of using the Gaussian 09 program were realized. The geometric optimization based on the B3LYP hybrid functional with the 6-31G base (d, p) was realized on bithiophene to sexithiophene. To reduce the calculation time, the alkyl chain is reduced to a propyl chain. Results are gathered in the table 1.

Table 1: HOMO/LUMO determination by geometric optimization of oligomers of 3-alkoxy/3-thioalkoxy-4-cyanothiophene

Oligomers	Chain	HOMO (eV)	LUMO (eV)	Gap (eV)	Average torsion angle (°)
Dimer	alcoxy	- 6.13	- 2.23	3.90	4
	thioether	- 6.37	- 2.24	4.13	45
Trimer	alcoxy	- 5.82	- 2.60	3.22	1
	thioether	- 6.36	- 2.55	3.81	45
Tétramer	alcoxy	- 5.67	- 2.80	2.87	2
	thioether	- 6.34	- 2.71	3.63	43
Pentamer	alcoxy	- 5.51	- 2.88	2.63	2
	thioether	- 6.05	- 3.00	3.05	28
Hexamer	alcoxy	- 5.51	- 3.01	2.50	1
	thioether	- 5.94	- 3.15	2.79	19

For alkoxy derivatives, the geometric modeling of each oligomer leads to a flat structure with an S--O interaction. In the case of oligomers with the thioether chain, geometric modelling for dimer, trimer and tetramer predicts a non-planar molecule with a torsion between each thiophene due to a repulsion between sulphurs. In the cases of pentamer and hexamer, the modelling leads to a much flatter carbon skeleton, which leads to a significant decrease in the HOMO-LUMO energy gap compared to the previous cases. These data are very well illustrated by the theoretical representations of trimers and hexamers in which no torsion is visible with alkoxy side chain (figure 3a-b) while thioalkoxy side chain (figure 3c-d) causes skeletal torsion.

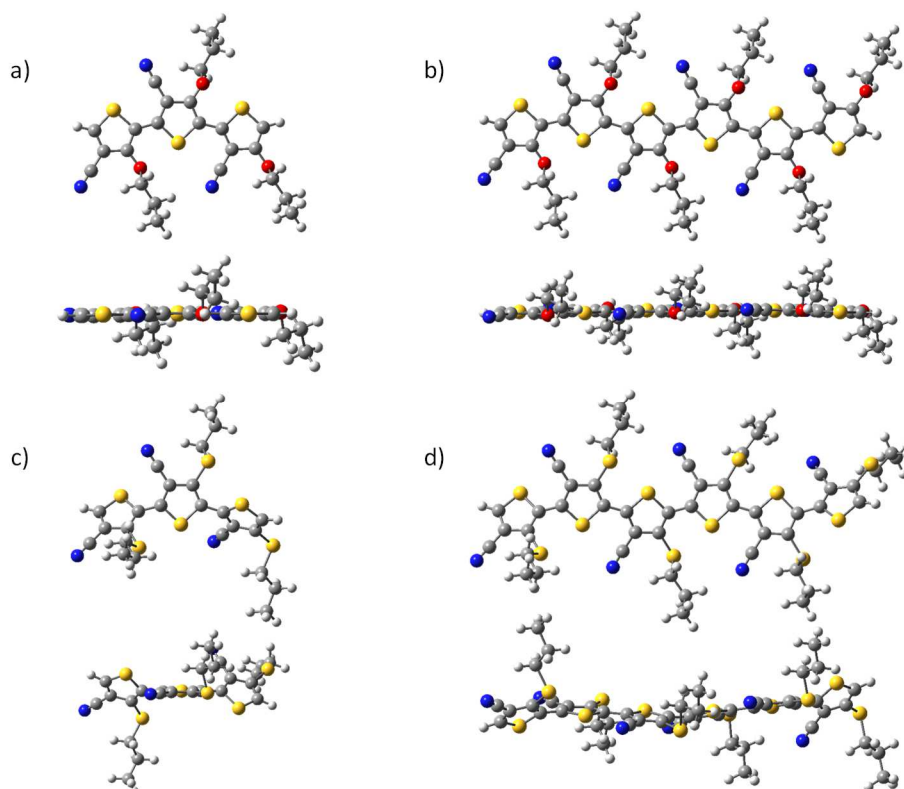


Figure 3: Theoretical structure of the trimer and hexamer with an alkoxy chain (a and b) and with a thioether chain (c and d).

The band gap energies were first estimated from UV absorption spectra by measuring the change in optical absorption. Band gaps extrapolated from the foot edge of the absorption bands are 1.50, 1.51 and 1.92 eV for **poly 4b**, **poly 4c** and **poly 7b** respectively. The band gap energies were also determined by electrochemistry and show results consistent with the optical gaps (see table 2). We also plotted ΔE as a function of $1/n$ (figure 4) to determine theoretical band gaps. We were able to estimate that the theoretical gap of poly(alkoxycyanothiophene) **4** was 1.80. The regression line for poly(thioalkoxycyanothiophenes) is less demonstrative due to the lower flatness of the small oligomers and the estimated ΔE is 2.38 eV. All these results are consistent with experimental data. The cyclic voltammograms of the **poly 4b** and **poly 4c** polymers are similar and have two reversible oxidation waves at 0.74 and 0.70 V respectively for the first wave and 1.34 V and 1.10 V for the second (table 2). The **poly 7b** polymer is irreversibly oxidizable at 1.42 V. In reduction, the **poly 4b** and **poly 4c** polymers have irreversible peaks at -1.45 and -1.39 V respectively, for **poly 7b** the reduction is almost reversible at -1.57 V. The **poly 4b** and **poly 4c** polymers which differ only with the alkyl chain have equivalent electrochemical properties. On the other hand, the substitution of oxygen by sulphur increases the oxidation and reduction potential by about 700 mV and 150 mV respectively. The more difficult oxidation of **poly 7b** can be explained by the more electron-donating thioether chain and by unfavorable S---S interactions that reduce conjugation. Considering the onset of oxidation and reduction waves, the HOMO and LUMO levels can be determined experimentally and are shown in Figure 5.

Table 2: Electrochemical results on polymers **poly 4b-4c-7b**

Compounds	E_{ox}^{a} (V)	$E_{\text{red}}^{\text{a}}$ (V)	$E_{\text{HOMO}}^{\text{b}}$ (eV)	$E_{\text{LUMO}}^{\text{b}}$ (eV)	ΔE_{elec} (eV)	ΔE_{opt} (eV) ^c	ΔE_{th} (eV) ^d
Poly 4b	0.74 / 1.34	-1.45	-5.97	-4.13	1.84	1.50	1.80
Poly 4c	0.70 / 1.10	-1.39	-5.93	-4.12	1.81	1.51	1.80
Poly 7b	1.42	-1.57	-6.52	-4.09	2.43	1.92	2.38

^a **poly 4b-c, poly 7b** deposited on the electrode in 0.1 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$, $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$, Pt electrode, ref. Fc/Fc^+ . ^b Using an offset of -4.99 eV compared to SCE.^[19] ^c Band gaps extrapolated from the foot edge of the absorption bands. ^d Determined from fig 4 by extrapolation of plot $\Delta E = f(1/n)$.

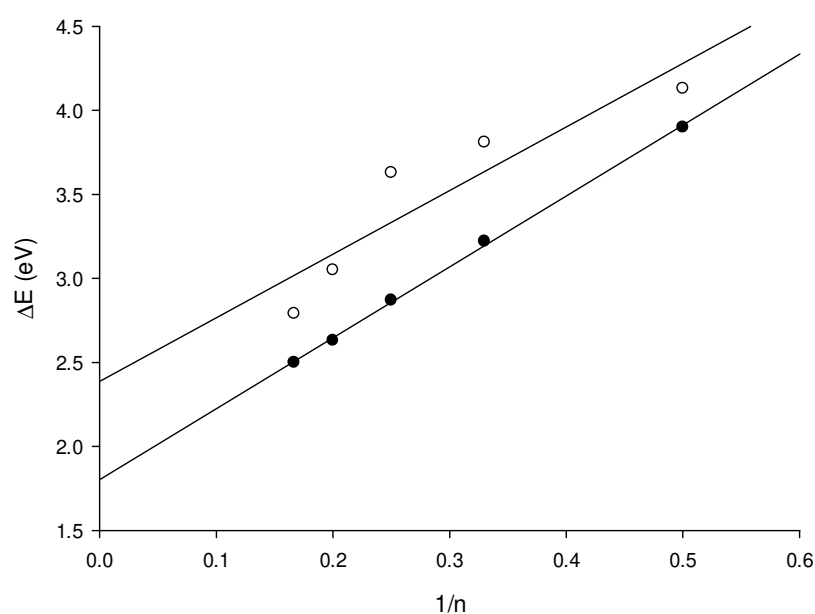


Figure 4: Band width evolution as a function of $1/n$ where n is the number of monomer in the molecule. Full circle: alkyloxycyanothiophene unit and empty circle: thioalkoxycyanothiophene unit

HOMO/LUMO levels are stabilized relative to P3HT showing the importance of thiophene substitution whatever the data we are taking into account.^[20] Sulphur is much more stabilizing than oxygen and cyano has a comparable effect regardless of the polymers. These energy levels would be interesting to use these materials as acceptors rather than donors in solar energy conversion devices.

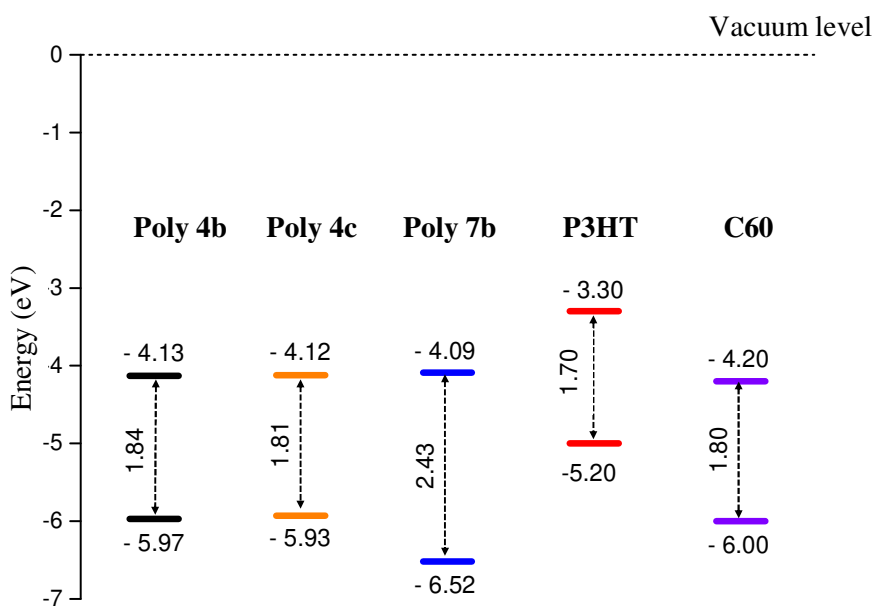


Figure 5: Experimental HOMO/LUMO levels of **Poly 4b**, **Poly 4c** and **Poly 7b** compared to P3HT.

4. Conclusion

In conclusion, several 3 and 4 substituted polythiophenes with donor and acceptor groups in these positions have been obtained. These groups will greatly influence the electrooptical properties of the final material since spectral coverage is very wide in the presence of an alkoxy group in position 3 whereas in the presence of thioalkoxy, this coverage is lower. The break-up of the conjugation seems to be responsible for this difference. On the other hand, HOMO/LUMO levels have been affected by these substitutions, and these levels are far from levels of the P3HT, thus attempts to use these materials as donors or acceptors will be considered in future works.

Acknowledgements

We thank the university of Angers for Jérémie Grolleau's grant.

References

- [1] aR. D. McCullough, R. D. Lowe, *Journal of the Chemical Society, Chemical Communications* **1992**, 70-72; bR. Miyakoshi, A. Yokoyama, T. Yokozawa, *Journal of the American Chemical Society* **2005**, *127*, 17542-17547.
- [2] aM. A. Baker, C.-H. Tsai, K. J. T. Noonan, *Chemistry – A European Journal* **2018**, *24*, 13078-13088; bin *Synthetic Methods for Conjugated Polymers and Carbon Materials*, pp. 59-95.
- [3] a) D. Alberico, M. E. Scott, M. Lautens, *Chem Rev* **2007**, *107*, 174-238; b) M. Wakioka, F. Ozawa, *Asian Journal of Organic Chemistry* **2018**, *7*, 1206-1216; c) H. Bohra, M. Wang, *Journal of Materials Chemistry A* **2017**, *5*, 11550-11571.
- [4] J. T. Blaskovits, M. Leclerc, *Macromol Rapid Comm* **2019**, *40*, 1800512.
- [5] aQ. Pierluigi, F. Andrea, *Letters in Organic Chemistry* **2018**, *15*, 991-1006; bJ. Roncali, *Chem Rev* **1992**, *92*, 711-738.
- [6] Y.-Y. Lai, T.-C. Tung, W.-W. Liang, Y.-J. Cheng, *Macromolecules* **2015**, *48*, 2978-2988.
- [7] S. Hayashi, Y. Kojima, T. Koizumi, *Polymer Chemistry* **2015**, *6*, 881-885.
- [8] C. L. Chochos, S. P. Economopoulos, V. Deimede, V. G. Gregoriou, M. T. Lloyd, G. G. Malliaras, J. K. Kallitsis, *The Journal of Physical Chemistry C* **2007**, *111*, 10732-10740.

- [9] C. Shi, Y. Yao, Yang, Q. Pei, *Journal of the American Chemical Society* **2006**, *128*, 8980-8986.
- [10] aA. E. Rudenko, P. P. Khlyabich, B. C. Thompson, *Acs Macro Lett* **2014**, *3*, 387-392; bA. E. Rudenko, P. P. Khlyabich, B. C. Thompson, *Journal of Polymer Science Part A: Polymer Chemistry* **2016**, *54*, 1526-1536.
- [11] S. Berson, S. Cecioni, M. Billon, Y. Kervella, R. de Bettignies, S. Bailly, S. Guillerez, *Sol Energ Mat Sol C* **2010**, *94*, 699-708.
- [12] J. Grolleau, F. Gohier, C. Cabanetos, M. Allain, S. Legoupy, P. Frère, in *Organic & biomolecular chemistry, Vol. 14*, Royal Society of Chemistry, Cambridge, **2016**, pp. 10516-10522.
- [13] P. G. Baraldi, G. P. Pollini, V. Zanirato, A. Barco, S. Benetti, *Synthesis* **1985**, *1985*, 969-970.
- [14] N. Hergué, C. Mallet, G. Savitha, M. Allain, P. Frère, J. Roncali, *Org Lett* **2011**, *13*, 1762-1765.
- [15] J. Grolleau, P. Frère, F. Gohier, *Synthesis* **2015**, *47*, 3901-3906.
- [16] M. Se´vignon, J. Papillon, E. Schulz, M. Lemaire, *Tetrahedron Letters* **1999**, *40*, 5873-5876.
- [17] M. Turbiez, P. Frère, M. Allain, N. Gallego-Planas, J. Roncali, *Macromolecules* **2005**, *38*, 6806-6812.
- [18] aJ. Roncali, P. Blanchard, P. Frère, *J Mater Chem* **2005**, *15*, 1589-1610; bG. Conboy, H. J. Spencer, E. Angioni, A. L. Kanibolotsky, N. J. Findlay, S. J. Coles, C. Wilson, M. B. Pitak, C. Risko, V. Coropceanu, J.-L. Brédas, P. J. Skabara, *Materials Horizons* **2016**, *3*, 333-339; cH. Huang, L. Yang, A. Facchetti, T. J. Marks, *Chem Rev* **2017**, *117*, 10291-10318.
- [19] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv Mater* **2011**, *23*, 2367-2371.
- [20] aP. Acevedo-Peña, A. Baray-Calderón, H. Hu, I. González, V. M. Ugalde-Saldivar, *Journal of Solid State Electrochemistry* **2017**, *21*, 2407-2414; bS. Berson, R. de Bettignies, S. Bailly, S. Guillerez, B. Jusselme, *Advanced Functional Materials* **2007**, *17*, 3363-3370.

Submission of manuscript to Solar Energy

Photometrical analysis of Mirrored Light Pipe:
*from state-of-the-art on experimental results (1990-2019) to the proposition of
new experimental observations in high solar potential climates*

Bruno MALET-DAMOUR, Dimitri BIGOT, Stéphane GUICHARD and Harry BOYER

Contents:

- *Revised Manuscript*

Corresponding author:

Bruno MALET-DAMOUR

Physics and Mathematical Engineering Laboratory for Energy, Environment and Building (PIMENT)

University of La Reunion,

117, rue du Général Ailleret

97430 Le Tampon (France)

tél : 06 92 81 95 96

fax : 02 62 96 28 59

email : bruno.malet-damour@univ-reunion.fr

Photometrical analysis of Mirrored Light Pipe:

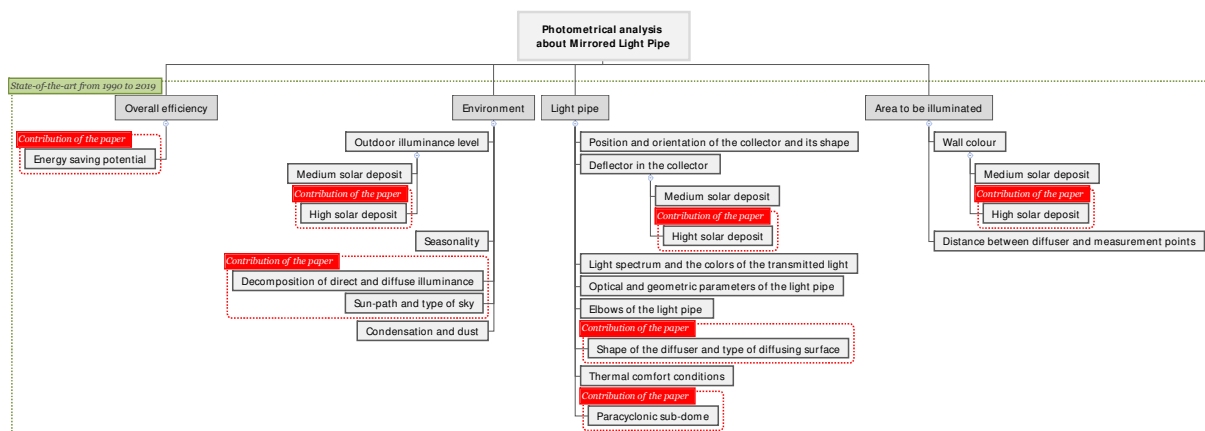
from state-of-the-art on experimental results (1990-2019) to the proposition of new experimental observations in high solar potential climates

Bruno MALET-DAMOUR¹, Dimitri BIGOT, Stéphane GUICHARD and Harry BOYER

University of La Reunion, Physics and Mathematical Engineering Laboratory for Energy, Environment and Building (PIMENT)
117, rue du Général Ailleret 97 430 Le Tampon, France.

1 : Phone +262 (0) 692 81 95 96, Fax (+262) 96 28 59, email : bruno.malet-damour@univ-reunion.fr

Graphical abstract :



Abstract :

This paper focuses on the part of Tubular Daylight Guide Systems (TDGS): the Mirrored Light-Pipe (MLP). MLP is part of the multiple specular reflection conveyors. They allow daylight to be transported and distributed in dark rooms far from traditional openings while limiting heat transmission. It involves collecting, concentrating, and diffusing sunlight using a dome placed on the roof. It is then conveyed through a highly reflective tube and diffused into a building's room using a diffuser.

Previous work (Malet-Damour et al., 2017, 2016) has shown that it was necessary to identify and study the climate in which the light pipe will be installed. A state-of-the-art of experimental and numerical results was conducted over the period from 1990 to 2019. It revealed that the behavior of the light pipe depends strongly on the indoor (area to be illuminated) and outdoor (meteorology) environment.

This paper presents the experimental observations of studies conducted from 2013 to 2015 on Mirrored Light-Pipe in Reunion Island. The climate in which the experiment was undertaken is presented with a focus on illuminance. In 2019, this study is the only one analyzing the performance of the light pipe in extreme situations of extreme sunlight conditions (maximum global illuminance of around 200 Klux). Experimental results based on various scenarios quantified the impact of the reflection coefficient of the area to be illuminated, the presence of an anticyclonic dome, the type of sky or the ideal position of a sub-dome deflector. The results are very encouraging.

31 **Keywords:** Mirrored Light Pipe; Experiment; Tubular Daylight Guide Systems; Review;
 32 Photometrical analysis; Daylight

33

34 Nomenclature

τ_{TDGS}	Transmission coefficient of the light pipe	[-]
ρ_{LP}	Internal reflectivity coefficient	[-]
ρ_{moy}	Average reflection coefficient of the walls test cell's	[-]
ρ_{PV}	Wall reflection coefficient	[-]
A_p	Aspect ratio, ratio between length L and diameter D of the light pipe	[-]
A_i	Reference of luxmeters position's inside the test cell	[-]
D	Euclidean distance (diffuser - point to illuminate)	[m]
DPF	Daylight Penetration Factor, ratio between indoor and outdoor illuminance	[-]
H	Vertical height of the diffuser	[m]
k_i	Brightness index	[-]

35 1. Introduction

36 Nowadays, due to climatic and energetic concerns, it is crucial to building sector to provide
 37 many solutions. The challenge is to limit the impact of buildings on energy consumption even more so
 38 greenhouse gas emissions which are responsible for global warming. That is why, it is essential to
 39 conduct investigations of passive lighting systems to use natural lighting as possible, to increase both
 40 visual and thermal comfort in buildings, and therefore help to reduce both light and HVAC energy use.
 41 From a health standpoint, artificial lighting tends to suppress melatonin production, thus ensuring
 42 increased vigilance and therefore, an improvement in work performance. The harmful effect is
 43 occupants cannot be in a serene surrounding. The intake of daylighting can balance this trend by
 44 ensuring a space of qualities both in production and in the occupant's welfare. In 1986, in Australia
 45 appeared the first innovative device in daylighting: the highly reflective light pipe, commonly known as
 46 MLP, for Mirrored Light Pipe. This technology seems to respond to energetic and health criteria. Light
 47 pipe allows daylight to be transported and distributed in dark rooms far from traditional openings. They
 48 offer the advantage of minimizing light loss while limiting heat transmission.

49 The behavior of a light pipe can be affected by 3 intrinsic factors and 1 external factor: (i) the
50 collection of daylight (via the collector) (ii) transmission (via the tube), (iii) diffusion (via the diffuser and
51 the area to be illuminated) and (iv) the environment (weather conditions, solar geometry, masks).

52 Light pipe has attracted considerable interest for nearly 30 years. Thanks to the beneficial effects
53 they provide: reduction in energy consumption, quality of transmitted light, limitation of heat input or,
54 architectural interests. In 1990, Tubular Daylight Guide Systems (TDGS) were judged by Littlefair as the
55 most innovative technology in daylighting (Littlefair, 1990). Many experimental and numerical studies
56 have been carried out to understand the device better. As experience can guide modeling, we conduct a
57 literature review from 1990 to the present by targeting discovery points. The objective is to take stock of
58 experimental knowledge about the light pipe and contribute to the understanding.

59 **1.1 Overall efficiency of the light pipes and energy-saving potential**

60 In 1997, Shao (Shao et al., 1997) presented an experimental study on the performance of light
61 pipe in the United Kingdom during the winter season. They showed that the potential for energy saving
62 is nearly 30 %, and can even increase significantly in the summer period thanks to day length.

63 Oakley continued the study by highlight the performance of 6 light pipes installed in 3 different
64 areas (store, office, and housing) in Leicestershire, England (Oakley et al., 2000). The results showed
65 that the most effective light pipe is straight, short with a low aspect ratio A_p . The author has noted that
66 if the diameter increases, the device will probably be more efficient. It also highlights the impact of the
67 light pipe on the energy savings achieved. For example, for an office which required lighting level (300
68 lux), it could be provided whole of the day by the light pipe. Oakley also pointed out that the device
69 affects user satisfaction with the visual comfort that creates a healthier environment.

70 Based on a coupling of light pipe and artificial lighting (LED), Ji (Ji et al., 2016) studied and
71 improved by simulation, an underground car park at Dalian Nationalities University of China. The
72 author showed that the hybrid lighting system allows an annual energy saving of 60.4 %.

73 The same year, Malet-Damour (Malet-Damour et al., 2016) proposed to compare the
74 performance of the light pipe to traditional artificial lighting. It was noted that in a clear sky, the light
75 pipe could deliver the equivalent of 10 incandescent bulbs or 5 compact fluorescent bulbs. The light

76 pipe provides an energy savings of 560 Wh, where artificial lighting is only be used 43% of the time (for
77 a halogen bulb of 70 W).

78 Other studies have also shown the potential of light pipe (Li et al., 2010; Samuhatananon et al.,
79 2011; Su et al., 2012; Thakkar, 2013; Wu and Li, 2012).

80 1.2 Parameters related to the illuminated area: colors and dimensions

81 The wall colors have a notable impact on light distribution due to reflection phenomena.
82 Indeed, the better the reflection coefficient, the higher the number of reflection of incoming light ray
83 (Descartes law), the better light distribution.

84 This observation allows to adapt the configuration of the room to limit sunspot or dark zone
85 inside, and improved light distribution on the whole workplane. Opposite, dark colors increase the
86 absorption coefficient.

87 In 1997, Shao (Shao et al., 1997) studied the performance of a light pipe under overcast or clear
88 skies. He showed that the color of the walls of the illuminated area had a substantial effect on the
89 internal illuminance. As a comparative element, he defined the ratio of indoor to global outdoor
90 illuminance. For a white room, this ratio is on average 14 % (under overcast conditions). For black walls
91 and the same weather conditions, this ratio can be as high as 4 %. A ratio of 7 % for white walls versus 2
92 % for black walls is also announced for clear sky conditions.

93 This trend is verified in a parametric analysis conducted by Zhang in 2002 (Zhang, 2002) but
94 remains very limited. Indeed, using the DPF model as also described in (Malet-Damour et al., 2016),
95 Zhang specified that its influence does not exceed more than 5 % in the indoor lighting balance.

96 In 2006, Chella (Chella et al., 2006) proposed a comparative study between the results of
97 numerical and experimental analysis (reduced scale with an artificial sky) for different wall reflectivities
98 (light and dark). The software used for this study were ADELIN 3.0 (International Energy Agency,
99 2002), ENERGY PLUS (DOE et al., 2016) and ECOTECT (Autodesk, 2008). The authors also
100 considered 2 types of sky: clear and overcast. For a clear sky, Chella showed that indoor reflected
101 component has an impact ranging from 19.4 % to 37.8 % (depending on the position in the place).

102 As for the geometric aspect, Zhang (Zhang et al., 2002) showed that the performance of the
103 tubular device depends strongly on (i) the Euclidean distance D and (ii) the vertical height of the
104 diffuser H . The author demonstrated that in real-life situations, the diffuser of the light pipe reacts more
105 like a point source than a finite surface. The illumination achieved inside the room is proportional to
106 $(H/D)^{1/3}$ and inversely proportional to D^2 (Bouguer's law).

107 1.3 Parameters related to the light pipe

108 In this section, it was noted in the literature that parameters relatives to the light pipe have a
109 notable impact on the quality or quantity of transmitted light. The light pipe could be considered as a
110 black box with several parameters which can affect the light collection, distribution, and quality. Among
111 them (i) the position and inclination of the collector (ii) the presence of dome deflector (iii) the type of
112 surface for the tube straight or elbowed and (iv) the nature of diffuser has been studied since 2002.

113 1.3.1 Impact of the position and orientation of the collector and its shape

114 In 2008, Wu (Wu et al., 2008) conducted an experimental analysis of the performance of 1
115 lateral and 2 zenithal light pipes. Measurements were taken at the same time for each process under real
116 weather conditions (sunny winter day in Beijing, China). If no masks obstruct access to daylight, the
117 results showed that the lateral light pipe offers better results than the zenithal device. A similar study
118 carried out by Duc Hien showed the efficiency of a collector placed on the façade was also (Duc Hien
119 and Chirarattananon, 2009).

120 In 2012, Kocifaj (Kocifaj et al., 2012) published a study demonstrating the optimal
121 configuration to take advantage of the nominal efficiency of a bent light pipe. It specifies that maximum
122 efficiency is achieved when the collector is oriented towards the solar path and pointed towards the sun.
123 It showed that straight pipe with horizontal collectors is less efficient than a light pipe with a collector
124 inclined towards the sun for clear skies. However, in cloudy skies, the straight pipe captures more of the
125 celestial illuminance.

126 Sharma (Sharma et al., 2018), with a numerical analysis, studied the optimal geometric shape of
127 the collector. The study showed that a 6° angle of inclination in the lower part of the collector increases
128 the performance of the device.

129 1.3.2 Impact of a deflector in the collector

130 Additional accessories, as light deflector associated with the light collection, increase light
131 capture and significantly improve the efficiency of the light pipe. Azad (Azad and Rakshit, 2018)
132 highlighted the impact of this process on the performance of the light pipe in India. He showed that
133 changing the position of the light deflector can improve the efficiency of the device by more than 2 %.

134 1.3.3 Link between the light spectrum and the colors of the transmitted light

135 The light intensity of a source influences the qualitative perception of ambiances. However, the
136 color of the light delivered has an essential aspect. It is generally assumed that the spectral variations
137 generated by MLP devices do not affect the color of the transmitted light. In 2014, Nilsson (Nilsson et
138 al., 2014) studied and confirmed this hypothesis using spectrophotometer measurements and numerical
139 study for direct and diffuse illuminance. It should be noted that the author ignored the collection and
140 diffusion mechanism. The MLP appears to have achromatic properties.

141 1.3.4 Impact of optical and geometric parameters of the light pipe

142 In 1998, Shao (Shao et al., 1998) studied the performance of light pipe installed in a dozen
143 buildings in the United Kingdom. The performance of the devices was evaluated for 4 types of
144 buildings. The light pipe all had a moderate aspect ratio A_p , and allowed indoor illuminance greater
145 than 450 lux, with a DPF of about 1 %. It is reduced by 0.1 % in the case of a thin and long pipe with
146 an elbow. The author concluded that large diameter pipe should be used as often as possible.

147 A few years later, Ellis (Ellis et al., 2004) showed the influence of the aspect ratio A_p on the
148 transmission coefficient τ_{TDS} for several light pipe reflectivities. Indeed, in his inter-software
149 comparative study (ENERGY PLUS (DOE et al., 2016) VS. FSEC (McCluney, 2003)), he found that the
150 increase in the aspect ratio causes an exponential drop in transmittance. For example, for a ρ_{LP}
151 reflectivity of 98 %, the transmission coefficient increases from 96 % ($A_p=2$) to 88 % ($A_p=8$). The
152 decrease is all the more significant as the reflectivity of the pipe decreases: at $\rho_{\text{LP}} = 92$ %, for an A_p going
153 from 2 to 8, the variation of the transmission coefficient amounts to more than 27 %. Ellis showed that
154 the length of the pipe mainly influences the aspect ratio.

155 For a given solar altitude and brightness index, the square radius of the tube affects the amount
156 of incoming light. Also, the aspect ratio of the light pipe and the solar altitude influence the
157 transmittance of the device (Zhang et al., 2002).

158 Maňková's study could support the conclusion of Ellis. The author surveyed MLP straight light
159 pipe (Maňková et al., 2009). He showed the impact of geometric and optical parameters (diameter,
160 length of the pipe, reflectivity) on the light transmission efficiency numerically. Under direct
161 illuminance (clear sky type), as the diameter of the tube increases, the efficiency of the device increases
162 logarithmically. Thus, tube diameter of 20 cm generates a transmission coefficient τ_{TDCS} of 80 %
163 compared to 87.5 % for a pipe of 80 cm. Also, when the reflectivity ρ_{LP} increases, the efficiency increases
164 linearly ($\tau_{\text{TDCS}} = 71.5$ % for a tube with a ρ_{LP} of 94 %, against 92 % for a reflectivity of 99 %).

165 On the other hand, the increase in the length of the pipe leads to an exponential decrease in
166 luminous efficacy. A 1.0 m long tube results in a transmission coefficient τ_{TDCS} of 89 % compared to 58
167 % for a pipe length of 5.0 m. The observation remained the same for diffuse illuminance (overcast sky),
168 but less pronounced than for direct part. Maňková specified that these results are validated for the type
169 of pipe studied and can evolve according to the reflectivity of the tube.

170 1.3.5 Impact of elbows of the light pipe

171 Based on straight and curved pipes (with a single elbow) and for elliptical or rectangular
172 sections, Gupta (Gupta et al., 2001) have numerically studied this problem. He performed a ray-tracing
173 simulation with variations in the radius of curvature. Gupta found that light propagation within the
174 tube is concentrated in the central part for a straight section while it is predominant on the inner
175 periphery for a section with an elbow.

176 In 2002, Carter (Carter, 2002) set up a study allowing him to compare experimental (in situ and
177 laboratory) and predicted data for the performance of different light pipe configurations. Carter found
178 that an elbow with an angle of 0 to 30 ° results in a loss of efficiency of nearly 20 % (at 30 °, -20 %).
179 Between 30 ° and 90 °, the decrease in efficiency is smaller (about 5 % from 30 ° to 90 °).

180 The same year, Zhang (Zhang, 2002) showed that the light loss associated with the use of a 30 °
181 bend was 20 % under overcast conditions. Similarly, Jenkins and Muneer (Jenkins and Muneer, 2004)

182 conducted a sensitivity analysis on the use of bent light pipe for 30 °, 60 °, and 90 ° inclinations. They
183 found a slight difference in performance between these devices. They deduced an exponential
184 relationship reflecting the losses associated with the transfer within the elbows.

185 In 2005, to model the performance of a light pipe, Jenkins (Jenkins et al., 2005) continued their
186 study on the impact of elbows. He deduced a ratio of equivalence between the singular light loss caused
187 by an elbow and the linear light loss of a straight pipe. Using experimental measurements on bends
188 from 5 ° to 75 °, Jenkins proposed an equation to calculate the percentage loss for curves at the same
189 angle. The year before, Van Derfolske and Hough (Van Derlofske and Hough, 2004) also studied the
190 impact of elbows on light transmission through the light pipe. They found that a 50 ° bend results in a
191 loss of flux of nearly 50 % while two 25 ° bends result in a loss of only 36 % of the luminous flux. The
192 ratio between the bending and the light loss is not linear.

193 The CIE report (CIE, 2006) on the efficiency of light pipes recommended the use of a standard
194 1.0 m long tube and the measurement of incoming and outgoing light fluxes. In this report, the experts
195 used fluorescent lamps mounted on panels incorporating a sphere and 2 pipes connected by an elbow.
196 Several elbow angles were selected for the study (0 °, 30 °, 60 °, 90 °, 2x30 °, and 2x90 °).

197 Su (Su et al., 2012) conducted an experimental study on commercial light pipes under real
198 climatic conditions contradicting previous results. The experimental results showed that, at equal
199 dimensions, the luminous flux at the exit of the curved light pipes is higher than the straight pipes for
200 clear sky conditions. The results are confirmed numerically. The number of hours of illuminance
201 accumulated between a straight and curved pipe also varies. The bent pipe is more efficient for luminous
202 fluxes greater than 2000 lm. Below this value, the straight and curved pipes are equal.

203 1.3.6 Impact of the shape of the diffuser and diffusing surface

204 Zhang (Zhang et al., 2002) tested the impact of the type of diffuser on the evolution of the DPF.
205 To do this, the author experimented with a straight diffuser and a curved diffuser. He noted that the
206 DPF reached with the flat diffuser is higher than that achieved with the curved diffuser.

207 In 2008, Wu (Wu et al., 2008) experimentally studied 2 types of diffusers: a prismatic diffuser
208 (diamond type) and an translucent diffuser (snow type). Experimental data showed that the light pipe

209 equipped with the translucent diffuser achieves better performance than the device with the prismatic
210 diffuser.

211 A study similar to that of Wu was also conducted by Baroncini (Baroncini et al., 2010). He
212 tested 2 types of polycarbonate diffusers, one characterized by a prismatic geometry, the other
213 characterized by a radial geometry, but completely transparent in the center. The conclusions were the
214 same as those of Wu.

215 Kennedy (Kennedy and O'Rourke, 2015) proposed and tested a new form of vertical light pipe
216 containing lateral openings serving several levels of a building.

217 1.3.7 Impact on thermal comfort conditions

218 Williams (Williams and Dorville, 2014) experimentally studied the thermal performance of light
219 pipe in a seminar room located in Beijing, China. The results showed that a significant temperature
220 gradient during the day could increase energy consumption to maintain a temperature of 25 °C. Indeed,
221 in clear sky, the diffuser temperature was 6.68 °C higher than the ambient temperature, and the
222 collector nearly 4.45 °C warmer than the diffuser. At night, the author showed that the light pipe
223 behaves like a thermal bridge because the temperature of the dome is always lower than the diffuser
224 temperature and the room temperature at night.

225 1.4 Parameters related to the environment of the light pipe

226 1.4.1 Impact of outdoor illuminance level and seasonality

227 The behavior of a daylighting device depends naturally on solar radiation. Callow (Callow,
228 2003), during this thesis, achieved a parametric analysis of the performance of light pipes. His
229 measurements were made in Nottingham and Singapore, and allowed to develop models for evaluating
230 the effectiveness of light pipes. He concluded that the efficiency of the light pipe was not always
231 proportional to the external illuminance.

232 A few years later, Li (Li et al., 2010) continued the analysis, and experimentally studied the
233 performance of straight light pipes equipped with sensors inside positioned according to different radii
234 of a circle. It showed that the transmittance of the device is not a constant value for a given pipe. It

235 varies according to the amount of external illuminance. In this case, device efficiency (defining by the
236 ratio between the outgoing and incoming luminous flux) ranged between 0.14 and 0.27.

237 Two years later, Kocifaj (Kocifaj et al., 2012) confirmed these results and showed the effect of
238 seasonality on the behavior of the light pipe. In summer, the average luminous flux under the light pipe
239 elbowed is only slightly higher than the luminous flux with a straight tube. In spring and autumn, it
240 increases. For temperate climates, the author has also concluded that the devices transmit more light if
241 they are curved.

242 Based on experimental data, Vasilakopoulou (Vasilakopoulou et al., 2017) analyzed the spatial
243 and temporal variability of indoor lighting using clustering techniques. There is an exponential
244 relationship between average and maximum indoor and outdoor illuminance levels.

245 1.4.2 Impact of solar altitude, sky brightness index and angle of incidence of the
246 incoming beam

247 Zhang (Zhang et al., 2002; Zhang and Muneer, 2000) and Carter (Carter, 2002) experimentally
248 studied the impact of solar altitude on the transmittance of the device. This meteorological parameter
249 modifies the number of inter-reflections within the tube. As the solar altitude increases, the number of
250 inter-reflections decreases, resulting in better transmittance. Wu (Wu et al., 2008) considered that solar
251 altitude is the main factor affecting the performance of the light pipe. He concluded that the light
252 distribution in a clear sky is asymmetrical and depends on the position of the sun. Zhang also pointed
253 out that the brightness index k_t and solar azimuth can also affect indoor daytime illuminance,
254 depending on the light pipe configuration (confirmed by (Darula et al., 2010)). In the tropics, the
255 luminous efficiency of the light pipes is better due to the predominant high solar altitude and long
256 sunshine duration. On the other hand, in temperate climates, and particularly in winter, these 2
257 parameters do not make possible to take advantage of the performance of a light pipe, although
258 necessary during this period (Darula et al., 2010).

259 Hansen (Garcia Hansen et al., 2009) showed that solar altitude impacts the angle of incidence
260 of incoming rays. The light loss in a tube is related to the multitude of reflections that the wave
261 undergoes. Consequently, a light beam with the most significant angle of incidence minimizes the

262 number of reflections and thus improves the performance of an MLP device. There are 2 solutions to
263 achieve this objective: (i) expand the system components or (ii) improve the collection system. This
264 finding was confirmed by Darula (Darula et al., 2010). Edmonds (Edmonds, 2010) also discussed
265 another aspect of the impact of the angle of incidence of penetrating rays. The variation of this angle has
266 a significant impact on the efficiency of the light pipe that can be related to the angular dependence of
267 the reflectivity on the Fresnel surface (perfect smooth mirror). The trend is verified and confirmed
268 through Swift's study (Swift, 2010). It showed that the transmittance of the light pipe decreases
269 significantly during months when the incidence angles of penetrating rays are low (winter).

270 Few years later, Vasilakopoulou (Vasilakopoulou et al., 2017) used a statistical approach
271 (clustering analysis) to confirm the existence of a correlation between the overall transmittance of the
272 light pipe, the solar azimuth and the solar altitude in clear sky.

273 In 2018, Tsang (Tsang et al., 2018) confirmed Edmonds and Swift results by also specifying that
274 light transmission is a monotonous function of solar altitude, except for low angles (winter, beginning,
275 and end of the day).

276 1.4.3 Dissociate direct and diffuse illuminance

277 As we have seen in the last section, the type of sky has a notable impact on light distribution.
278 Consequently, it is necessary to decompose the direct (significant in clear sky) and diffuse (major in an
279 overcast sky) illuminance.

280 In 2009, Mohelnikova (Mohelnikova, 2009) conducted a study on a straight light pipe. It
281 showed that the luminous flux at the diffuser outlet and the distribution of illuminance under the
282 diffuser is uniform and symmetrical when the sky is overcast. In clear skies, this distribution is not
283 directly uniform.

284 Two years later, Lo Verso (Lo Verso et al., 2011) showed with simulations under SkyVision that
285 it is more accurate to decompose light (direct and diffuse). He justified it by means of an experiment on
286 a Mirrored Light Pipe for 2 types of sky (overcast and clear).

287 The distinction between clear and overcast skies can be made by the solar altitude whose the
288 influence in the clear sky is notable. Oh (Oh et al., 2013) showed using a diagram "Candela power

289 distribution curve - CDC" that the light distribution of the light pipe is directly related to the solar
290 altitude. He concludes that the light pipe uses all the components of daylight (diffuse and direct), but
291 that direct light influences the light distribution.

292 1.4.4 Impact of condensation and dust

293 Dust and condensation that may form in light pipes can affect their performance. Wu (Wu et
294 al., 2012) experimentally studied this link by measuring the transmitted luminous flux under 3 different
295 conditions (cleanliness, dust, and condensation) and for clear and overcast sky conditions. The results
296 showed that dust has a more significant impact on the performance of the device than condensation. In
297 clear skies, condensation reduces transmission by 6.37 % compared to 15.31 % for dust. In overcast
298 conditions, the cleanliness of the dome results in a reduction of 24.05 % compared to 17.2 % for
299 condensation.

300 1.5 Variability of all parameters

301 In 1995, Swift and Smith (Swift and Smith, 1995) studied the links between the design and
302 material parameters for a circular MLP device. They calculated the transmission coefficient precisely by
303 using an optical analysis of the propagation of light rays along a tube. The authors derived an equation
304 involving the reflectivity of the pipe, aspect ratio, and angle of incidence of incoming rays. This study
305 clearly showed that the performance of the light pipe depends on many parameters, which can
306 themselves vary considerably.

307 1.6 Originality of the paper

308 Table 1 summarizes all the studies identified from 1990 to 2019 and classified by theme.

309 All the studies reviewed were conducted under temperate or continental climatic conditions in
310 the Northern Hemisphere. These experimental conditions made it possible to evaluate the behavior of
311 the light pipes for nominal illuminance levels of around 100 Klux in clear sky. This paper presents the
312 only experimental data in the southern hemisphere (different solar path) and for extreme sunlight
313 conditions. In these climatic conditions, we come to refute, confirm, and bring a new perspective on the
314 behavior of the Mirrored Light Pipe. We demonstrated the close link between the type of sky, the solar
315 path, the indoor light distribution, and the lighting levels achieved. We also showed that the energy-

316 saving potential generated by the light pipe in tropical environments and associated with different colors
317 of the area to be illuminated. We also proposed an experimental analysis of the interest of a solar
318 concentrator placed in the dome of the device. We have also evaluated the impact on indoor lighting of
319 a mandatory device in cyclonic areas of the globe: the anticyclonic sub-dome.

320 All these results offer an additional step forward in the understanding of the behavior of the
321 Mirrored Tubular Daylight Guide Systems and contribute to the enhancement of this technology.

322 2. Materials and methods

323 As seen in the previous review, it is necessary to study the light pipe environments to
324 understand their behavior. Reunion Island is very particular due to his intense solar irradiation, that is
325 why, we choose to set up experimentation to verify and validate observations from the literature.

326 2.1 Experiment set-up

327 The measurements are carried out on an experimental cell, called LGI (Miranville, 2002), and
328 located in Saint-Pierre, Reunion Island. The arrangement of the empirical support has been made
329 considering the sun's path and promoting an orientation without obstacles to the wind. The LGI is
330 oriented North/North-West (9° N). Representing a small building of 9 m^2 , it consists of vertical opaque
331 walls made of composite panels, a glass door (north facade), a blind (hidden) and a horizontal ceiling.
332 The dimensions are described in Figure 1. The sloping roof (20°) is made of corrugated night blue sheet
333 metal. A Mirrored Light Pipe (SOLATUBE®) has been installed in the roof plane and is curved to
334 ensure the horizontality of the diffuser. The walls of the device have an internal reflection coefficient of
335 99.7 %. An impact study revealed that the far-mask effect was negligible.

336 2.2 Measurement and data acquisition

337 Daylight measurements are collected from AHLBORN type devices with their central data
338 acquisition systems. These devices are synchronized with each other and record at the time step of a
339 minute. The indoor illuminance is measured from 9 luxmeters, positioned as shown in Figure 2 so that
340 each sensor is located on a circle of different diameter whose center is A0. The workplane is fixed at 10
341 cm from the ground. The external luxmeters are used to measure global and diffuse illuminance (Figure
342 3). The measurement of diffuse illuminance is ensured by the shadow ring designed in the laboratory,

343 called SHADECO. The procedure of conception and validation of this device is described in (Malet-
344 Damour et al., 2018).

345 The test cell was adapted to correspond to each experimental scenario. By measuring indoor and
346 outdoor illuminances, it was tried to confirmed or refuted the findings reviews about the influence of
347 the type of sky on light distribution in the southern hemisphere. That is why the wall colors have been
348 colored to black (deleted the reflection part of diffusing light). Also, by changing wall colors, it was
349 possible to understand the impact of this parameter (the reflection coefficient) on the light level. Other
350 scenarios were conducted to quantify the effects of 2 devices used to improve light collection (changing
351 the position of a reflector in the dome) or to protect the light pipe (anticyclonic sub-dome).

352 All experimental scenarios were synthesized in Table 2.

353 3. Results and discussion

354 3.1 Solar deposit of climate study

355 We carry out a brief climatic analysis of the environment in which the light pipe is positioned.
356 The objective is to understand the solar potential of the city of Saint Pierre, Reunion Island. We seek to
357 discern the annual evolution of the global outdoor illuminance measured with an external luxmeter.

358 Figure 4 highlights a significant seasonality in global illuminance corresponding substantially to
359 the seasons present in Reunion Island. The southern summer extends from November to April. This is
360 the period when the solar deposit is most abundant. The days are longer, with a maximum illuminance
361 frequently between 150 Klux and 200 Klux (in clear sky), and the beginning and end of the day close to
362 50 to 75 Klux.

363 The southern winter, from May to October, is the period when the maximum illuminance is
364 around 100 to 125 Klux. The days are shorter. Mornings and ends of the days provide less than 75 Klux
365 of light. The trend changes as early as August when the days recover from hours of sunshine.

366 Seasonality does not seem to be properly related to the lighting needs. Indeed, a system using
367 daylight within a building will offer significant efficiency from September to April, and less for the rest
368 of the year.

369 3.2 Impact of sky type on light distribution

370 The objective was to see the impact of the type of sky on the light distribution within the room
371 (see Table 2, scenario N°1). All the inner walls of the cell are covered with a black wallpaper (reflection
372 coefficient close to 0.05). The objective is to eliminate factors that can influence the light distribution
373 within the room. The part of the internal reflections being negligible, the light pipe is then the only light
374 source in the room (Figure 5).

375 The day of September 23, 2014 presents a clear sky with a maximum global outdoor
376 illuminance of 120 Klux. The contribution of the celestial vault is less than 17 Klux (see Figure 6). These
377 conditions are typical of sunny conditions for a clear day in winter on Reunion Island.

378 Under the diffuser (A0), we notice that the maximum values for indoor illuminance are not at
379 solar midday (marked by a vertical blue dotted line). When the global outdoor illuminance reaches its
380 maximum during the day, the light pipe does not generate an illuminance that can be considered as a
381 maximum in the area. Indeed, we can see that at this same time, the A1 sensor has illuminance values
382 close to 600 lux. The other sensors do not seem to show any particular event.

383 Overall, if we refer to the hourly evolution of the illuminance for each instrument, we see between 1
384 and 2 unsynchronized peaks of illuminance appear during the day. These events are localized. Their
385 evolution is linked to time and space. We assume that these are "sunspots" depending on the position of
386 the Sun.

387 The distribution of illuminance on the ground within the room is presented for different hours
388 (Figure 7). This mode of representation is commonly used in lighting thanks to the ease with which a
389 light distribution can be imaged on a work surface.

390 We select representative hours, where the indoor illuminance is important enough to allow us
391 to observe a phenomenon. At 9:00 am, the average illuminance is about 150 lux, and the light
392 distribution appears to be angularly uniform. In the following hours, the distribution no longer seems to
393 follow Lambert's law because the maximum illuminances change position over time. At 11:00 am in
394 particular, the maximum illuminance is located southeast while the Sun is oriented northeast. When the
395 Sun is in the axis of the light pipe (due North), the distribution seems to refocus around the central
396 point (under the diffuser in A0). The following hour we notice an opposite position to the 11:00 am

397 event: the maximum illuminance is located South-West while the Sun is located in the North-West axis.
398 The following hours resemble the first hours of the day by not marking any particular orientation in the
399 distribution of indoor illuminance.

400 In all likelihood, the position of the Sun impacts the light distribution, and more precisely,
401 direct illuminance does not follow the law of logical diffusion because the source moves during the day.

402 Visually, we can confirm these results. Figure 8 shows solar bands marked by more intense
403 illuminance. If a light band is positioned on one of the sensors, it will detect high illuminance without
404 the phenomenon being visible through the other instruments. Unlike Baroncini's findings (Baroncini et
405 al., 2010), these pictures clearly shows that the diffuser does not allow a distribution according to
406 Lambert's law. Maybe these solar bands are not high enough to be visible under lower solar irradiation.

407 To conclude, direct lighting is not distributed rigorously throughout the room. It is localized
408 and generates light bands with high illuminance levels. In a global approach, the phenomenon observed
409 being localized, it would be necessary to consider the global impact of these "sunspots".

410 We are now looking to visualize the photometric phenomena for an overcast day (November 30,
411 2014). As can be seen in Figure 9, the global outdoor illuminance follows the trend of diffuse part. A
412 maximum illuminance is recorded at 10:00 am and may correspond to a partial clearing of the clouds.
413 Otherwise, the outdoor global and diffuse illuminances are around 50 Klux between 9:30 am and 2:30
414 pm.

415 As the direct outdoor illuminance is close to zero, we notice that the time evolution at each
416 measurement point is similar (Figure 9). To justify this observation, we focus on an event (marked by a
417 red dotted vertical line). This event could correspond to the passage of a denser cloud. It is reflected
418 inside the cell at the same time. We find that the further away the measurement point is far from the
419 diffuser, the more the illuminance decreases proportionally. This behavior suggests a distribution from
420 an orthotropic light source.

421 Overall, we notice that in overcast skies, the daily evolution of indoor and outdoor illuminances
422 correctly follows the same progression.

423 Using the same methodology as for clear sky, we plot the evolution of light distribution within
424 the room for different hours (Figure 10). In the configuration of an overcast sky, the illuminance levels
425 achieved are much lower than those obtained in clear sky. The average deviation under the diffuser is
426 close to 200 lux.

427 During the hours of the day, the illuminance distribution does not change. At 9:00 am, the
428 illuminance in the center of the room increases (200 lux), then decreases in the following hours to
429 increase again at 1:00 pm. Overall, we confirm the observation made in the previous curves: the
430 luminance increases, but remains stable according to the direction of emission: the illuminance
431 distribution follows Lambert's law.

432 In conclusion, the light pipe can be considered as a black box that reflects the input/output
433 load, with one inversion. In this way, the diffusion within the room can be uniform in an overcast sky,
434 and directional in a clear sky in extreme solar irradiation environments.

435 **3.3 Impact of the color of the area to be illuminated: evaluation of the energy-saving** 436 **potential**

437 This study consists of varying the colors of the interior walls of the area to be illuminated and
438 understanding their impact on indoor lighting and artificial lighting autonomy (see Table 2, scenarios
439 N°1 to 5). We will use the average reflection coefficient to compare the different situations. This
440 parameter is calculated retain proportion to the surfaces of each color. We assume that the reflection
441 coefficients of the walls are constant and known: (i) white wall reflection coefficient: (ii) black wall
442 reflection coefficient: (iii) grey wall reflection coefficient: .

443 In this way, Table 2 shows the values of this parameter according to the experimental scenarios.

444 To take into account the impact of this parameter on the energy autonomy of the room, we
445 consider the room as an office which required a minimum lighting level of 200 lux (according to the
446 European standard EN 12 464-1). That's why we calculate the percentage of time the lighting level is
447 higher than needed.

448 Our reference will be scenario N°5 (5 white walls and 1 grey wall). We will compare events from
449 one year to another. The reference case data cover the years 2013 and 2014, while the other scenarios

450 were conducted from 2014 to 2015. By comparing the same dates for different years, we are assured that
451 the solar path is theoretically similar. Thus, the solar altitude and azimuth can deviate from the
452 influential parameters. We will use an hourly ratio of the average indoor illuminance (average of the
453 hourly illuminance recorded by the indoor luxmeters) to the outdoor global illuminance. This ratio gives
454 a general trend in the time evolution of illuminance in terms of usefulness, which excludes the impact
455 of direct part on the light distribution within the room. We select days with similar outdoor global
456 illuminance profiles from one year to the next.

457 **Comparison of scenarios N°1 and 5**

458 The days of November 21, 2013 and November 21, 2014 are clear sky days (Figure 11). The
459 hourly profile of outdoor global illuminance from one year to another is similar with a maximum
460 illuminance of around 131 Klux. The patterns of the ratios are related to a close coefficient: the part
461 with the highest reflection coefficient has the highest rate. Indeed, by increasing the average reflection
462 coefficient from 0.05 to 0.699, we increase the average indoor illuminance by 47 % on average. When
463 the cell has its black walls, the light pipe allows autonomy in lighting nearly 3 % of the time compared
464 to 37 % for the case study N°5. This means that 3 % of the time we are above 200 lux, the minimum
465 required level. As a result, the artificial top-up is inevitable 97 % of the time (in clear sky) compared to
466 63 % for a room with white walls.

467 **Comparison of scenarios 2 and 5**

468 March 16, 2015 is a clear day. The same day of 2014 is partially covered (Figure 12). These two
469 days have the most comparable profiles of the measurement period of study case N°2. The maximum
470 outdoor global illuminance is about 120 Klux. The pattern of the ratios of the studied cases is similar.
471 The increase in the average reflection coefficient from 0.162 to 0.699 increases the average useful indoor
472 illuminance by 42 %. The scenario N°2 allows being autonomous almost 10 % of the time compared to
473 32 % for the case N°5. For an area with 5 black walls and 1 white wall, artificial lighting is unavoidable
474 90 % of the time (in clear sky) compared to 68 % for a room with white walls.

475 **Comparison of scenarios 3 and 5**

476 The days of March 24, 2014 and March 24, 2015 are clear-sky days with a similar time profile
477 for global outdoor illuminance (Figure 13). The maximum illuminance is about 121 Klux. With one
478 factor aside, the ratios are similar. By increasing the average reflection coefficient from 0.274 to 0.699,
479 we increase the average indoor illuminance by 36 % on average and thus be energy self-sufficient 17.5 %
480 of the time compared to 39.8 % in case N°5. The use of artificial lighting is unavoidable 82.5 % of the
481 time (in clear sky) compared to 60.2 % for a room with white walls.

482 **Comparison of scenarios 4 and 5**

483 The days of April 3, 2014 and April 3, 2015 are also clear sky days with a similar time profile for
484 global outdoor illuminance (Figure 14). The maximum illuminance is about 113 Klux. Both days have a
485 ratio profile identical to a factor. By increasing the average reflection coefficient from 0.385 to 0.699, we
486 increase the average indoor illuminance by 35 % on average. It reduces the artificial lighting level to
487 82.3 % of the time (in clear sky) compared to 60.8 % for a room with white walls.

488 **Synthesis**

489 Overall, we find that the reflection coefficient of the walls has a considerable impact on the
490 average illuminance within the area. The more we have an area with clear walls, the more we will
491 increase the useful average illuminance. This is due to the absorption coefficient of the black walls,
492 considerably limiting the internally reflected illuminance.

493 This observation can be illustrated in Figure 15. By moving from a room with black walls to a room with
494 white walls, we can double the level of indoor illuminance and thus limit the use of an additional
495 artificial lighting system. This observation makes it possible to complete what the literature had revealed
496 to us in the previous section (Chella et al., 2006; Shao et al., 1997; Zhang, 2002).

497 **3.4 Impact of the position of a dome deflector**

498 In the southern hemisphere, the northern orientation is preferred to increase the performance
499 of solar devices. At the summer solstice (December 21), the Sun rises in the East/South-East and sets in
500 the West/South-West. At the winter solstice (June 21), the Sun rises in the northeast and sets in the
501 northwest. A deflector device, placed in the dome, maximizes the collection of solar rays.

502 We wanted to evaluate the impact of deflector positions on the amount of light inside the area
503 to be illuminated for the configuration of the light pipe studied (curved tube with the collector in the
504 plane of the roof). That is why, measurements were made by positioning the deflector in different
505 orientations (North, South, East, and West), as described in Table 2, with the scenarios N°6 to 9).
506 Figure 16 shows the different positions tested and the solar-path of the study city (Saint-Pierre,
507 Réunion). “North” orientation means that the deflector is facing south (back to the north).

508 Before identifying the most optimized orientation of the deflector to increase the collection of
509 solar rays, we seek to evaluate the impact of this device on the supply of daylight within the area to be
510 illuminated. We compare the effect of the deflector positioned to the South (facing the North,
511 orientation recommended by the manufacturer, scenario N°7) for a clear sky when the walls of the room
512 are black. The deflector-free measurements were obtained in December 2014. Measurements with
513 deflector are collected during February 2015, at the rate of one week of collection per orientation. To
514 rule out the impact of the solar-path, we will use the ratio between the useful average indoor and global
515 outdoor illuminance, averaged over the measurement period.

516 We can see that the deflector increases the amount of daylight (Figure 17). However, the device
517 does not significantly improve the performance of the light pipe.

518 Concerning the impact of the deflector orientation, and concerning the experimental data, we
519 find for each a clear measurement period, intermediate and cloudy sky days. Since the solar path is not
520 the same from one day to the next, and therefore from one configuration to another, we determine the
521 impact of the deflector position from an average ratio. This ratio is the ratio between the indoor and
522 global outdoor average illuminance during the period. With measurements in diffuse illuminance, and
523 neglecting the part of the reflected illuminance (no mask to consider), we obtain direct illuminance
524 (from the subtraction of diffuse from global illuminance). We apply an impact ratio to the previously
525 calculated average one by determining the proportion of diffuse and direct impact on indoor
526 illuminance. Then, we can learn, by orientation, two essential pieces of information (i) the relationship
527 between the position of the deflector and the overall efficiency (ii) the relationship between the
528 effectiveness of the deflector, its location and the type of illuminance (direct or diffuse).

529 Figure 18 confirms that positioning the deflector in the South (deflector facing North, scenario
530 N°7) increases the efficiency of the light pipe. The figures are still close for the North position (facing
531 South, scenario N°6) this being probably because the collector is inclined in the plane of the roof.
532 Moreover, at this time of year (see Figure 16, red line of the solar path), the Sun passes from East to
533 West with an almost similar part of the day when the collector sees the Sun in the South and North.
534 The East (scenario N°9) and West (scenario N°8) positions are optimal for capturing morning or late
535 afternoon light rays, respectively.

536 By looking at the differentiation of diffuse and direct illuminance, we can see that (i) direct part
537 has a more significant impact on the level of indoor illuminance for a deflector positioned in the South
538 (scenario N°7), (ii) diffuse part is predominant in the supply of light for a deflector in the North. For the
539 East and West orientations, diffuse and direct illuminances have a similar impact.

540 We deduce that it is preferable to orient the deflector to the North or South (in the case where
541 the collector is inclined to the North) for the Southern Hemisphere. This position can also change
542 during the year, depending on the weather conditions. Tropical summer is marked by more cloudy days
543 (predominant diffuse illuminance), the deflector could be placed in the North, and conversely in winter
544 (mostly clear sky).

545 **3.5 Tropical arrangement: impact of the anticyclonic sub-dome**

546 During a tropical cyclone, several extreme phenomena can damage or even destroy a structure
547 (wind gusts, torrential rain, floods, debris carried by wind or rivers, landslides, etc.). In general, an
548 anticyclonic construction is designed to withstand the direct effects of wind, airborne debris, and rain. It
549 is, therefore, a question of designing and building constructions with a sufficient level to ensure the
550 three essential functions: mechanical resistance, shelter from wind and rain. That is why it is necessary
551 to protect the fragile areas of a building. The technological difficulty is to establish a compromise
552 between resistance and tightness without hindering the primary function. The light pipe, because of its
553 position on the building represents a point of fragility. There is an anticyclonic sub-dome to compensate
554 for shocks related to flying debris. Reunion Island is one of the areas where this is necessary.

555 This case study (see Table 2, scenario N°10) is specific to geographical areas subject to
556 anticyclonic provisions. The sub-dome is installed on the light pipe, as shown in Figure 19. We are
557 trying to evaluate the impact of this sub-dome on the overall performance of the light pipe.

558 As before, we will base our analysis on the ratio between the average indoor and outdoor
559 illuminance. This will allow comparing days whose solar geometry will not be the same. We will examine
560 the average daily ratio for configurations with and without the anticyclonic sub-dome for a test cell with
561 black walls. We only use clear sky days to assess the maximum impact of the sub-dome.

562 We find that the anticyclonic sub-dome has an impact on the transmission factor of the light
563 pipe τ_{TDCS} (Table 3). This additive element reduces light transmission by an average of $9.2 \% \pm 3 \%$.
564 While it may be negligible for indoor illuminance achieved in clear sky, it will be essential to take into
565 account its contribution in the overcast sky.

566 **Conclusions and perspectives**

567 A literature review permitted to identify and to class each parameter, which could have an impact
568 on light pipe performance and light distribution inside the illuminated area. It was noted that
569 geometric, optic or climatic parameters relatives to (i) illuminated area (ii) light pipe (iii) environment of
570 the device, have a notable impact on indoor light distribution and light level. All the studies reviewed
571 were conducted under temperate or continental climatic conditions in the Northern Hemisphere.

572 This paper presents the only experimental data in the southern hemisphere (different solar path)
573 and for extreme sunlight conditions. It permitted to understand and apprehend the behavior of the
574 light pipe under the intensive climatic condition of Reunion Island. We found that the light
575 distribution within the room was strongly related to the type of sky. In cloudy skies, the diffuser behaves
576 like an orthotropic source whose diffusion follows a Lambertian law. Indeed, the light pipe acts as a
577 black box. The profile of the indoor illuminance is similar to the profile of the outdoor. In a clear sky,
578 the observation is no longer valid. The indoor lighting becomes directional, linked to the position of the
579 Sun. Lambert's law is no longer valid.

580 This work also allowed to test other experimental configurations such as the variation of the colors
581 of the illuminated area. We noted that the increase in the average reflection coefficient could result in a
582 significant increase in the average indoor illuminance. Energy autonomy is the most revealing parameter
583 of the study, showing that switching from a dark to a bright room avoided the use of an artificial light
584 source no less than 37 % of the time.

585 It was also studied the optimal position of a reflector placed in the dome to increase the collection
586 of solar rays. Reunion Island is located in the southern hemisphere at latitude 21 °S. In this region of
587 the globe, and given the sun path, it is common to orient solar devices to the North. The study
588 confirmed that our collector with deflector, inclined in the roof plane (20 °), is the most efficient when
589 facing North. A lack of orientation could lead to a drop of nearly 20 % in the light transmission of the
590 light pipe.

591 Considering the location and cyclonic concerns of Reunion Island, it was tried to evaluate the
592 impact of an anticyclonic sub-dome placed under the primary collector. Experimental results concluded
593 that it reduces 9.2 % of the average transmission of the light pipe.

594 This paper was intended to contribute to the experimental photometric study of Mirrored Light
595 Pipes. A thermal experimental study has starting to understand the impact of the light pipe on indoor
596 ambient conditions and the user thermal comfort in the tropical climate.

597 **References**

598 Autodesk, 2008. ECOTECH ANALYSIS.

599 Azad, A.S., Rakshit, D., 2018. Experimental Study of Tubular Light Pipe System: Influence of Light
600 Reflector on Its Performance, in: Sayigh, A. (Ed.), *Transition Towards 100% Renewable Energy: Selected Papers from the World Renewable Energy Congress WREC 2017, Innovative Renewable Energy*. Springer International Publishing, Cham, pp. 21–30. https://doi.org/10.1007/978-3-319-69844-1_3

604 Baroncini, C., Boccia, O., Chella, F., Zazzini, P., 2010. Experimental analysis on a 1:2 scale model of the
605 double light pipe, an innovative technological device for daylight transmission. *Sol. Energy* 84,
606 296–307. <https://doi.org/10.1016/j.solener.2009.11.011>

- 607 Callow, B.J., 2003. Daylighting Using Tubular Light Guide Systems. University of Nottingham.
- 608 Carter, D.J., 2002. The measured and predicted performance of passive solar light pipe systems. *Light.*
609 *Res. Technol.* 34, 39–51. <https://doi.org/10.1191/1365782802li029oa>
- 610 Chella, F., Zazzini, P., Carta, G., 2006. Compared numerical and reduced scale experimental analysis on
611 light pipes performances ., in: *Proceedings of the 5 Th International Conference on Sustainable*
612 *Energy Technologies {SET}*. pp. 1–6.
- 613 CIE, 2006. Tubular daylight guidance systems. Vienna. *Comm. Int. l'Eclairage* 173:2006, 3–38.
- 614 Darula, S., Kocifaj, M., Kittler, R., Kundracik, F., 2010. Illumination of interior spaces by bended
615 hollow light guides: Application of the theoretical light propagation method. *Sol. Energy* 84,
616 2112–2119. <https://doi.org/10.1016/j.solener.2010.09.003>
- 617 DOE, BTO, NREL, 2016. *Energy Plus*.
- 618 Duc Hien, V., Chirarattananon, S., 2009. An experimental study of a facade mounted light pipe. *Light.*
619 *Res. Technol.* 41, 123–139. <https://doi.org/10.1177/1477153508096167>
- 620 Edmonds, I., 2010. Transmission of mirror light pipes with triangular, rectangular, rhombic and
621 hexagonal cross section. *Sol. Energy* 84, 928–938. <https://doi.org/10.1016/j.solener.2010.03.001>
- 622 Ellis, P.G., Strand, R.K., Baumgartner, K.T., 2004. Simulation of Tubular Daylighting Devices and
623 Daylighting Shelves in Energyplus, in: *Conference, I-U.N. (Ed.), SimBuild 2004*. Boulder,
624 Colorado, pp. 1–8.
- 625 Garcia Hansen, V., Edmonds, I., Bell, J.M., 2009. Improving daylighting performance of mirrored light
626 pipes: Passive vs. active collection systems, in: *PLEA 2009 - Architecture Energy and the*
627 *Occupant's Perspective: Proceedings of the 26th International Conference on Passive and Low*
628 *Energy Architecture*. Quebec City, Canada.
- 629 Gupta, A., Lee, J., Koshel, R.J., 2001. Design of efficient LightPipes for illumination by an analytical
630 approach. *Appl. Opt.* 40, 3640–3648.
- 631 International Energy Agency, I., 2002. *ADELIN*E.
- 632 Jenkins, D., Muneer, T., 2004. Light-pipe prediction methods. *Appl. Energy* 79, 77–86.
633 <https://doi.org/10.1016/j.apenergy.2003.11.003>

- 634 Jenkins, D., Muneer, T., Kubie, J., 2005. A design tool for predicting the performances of light pipes.
635 Energy Build. 37, 485–492. <https://doi.org/10.1016/j.enbuild.2004.09.014>
- 636 Ji, S., Cao, G., Zhang, J., Yu, F., Li, D., Yu, J., 2016. Lighting design of underground parking with
637 tubular daylighting devices and LEDs. *Optik (Stuttg)*. 127, 1213–1216.
638 <https://doi.org/10.1016/j.ijleo.2015.10.189>
- 639 Kennedy, D.M., O'Rourke, F., 2015. Experimental analysis of a scaled, multi-aperture, light-pipe,
640 daylighting system. *Sol. Energy* 122, 181–190. <https://doi.org/10.1016/j.solener.2015.08.013>
- 641 Kocifaj, M., Kundracik, F., Darula, S., Kittler, R., 2012. Availability of luminous flux below a bended
642 light-pipe: Design modelling under optimal daylight conditions. *Sol. Energy* 86, 2753–2761.
643 <https://doi.org/10.1016/j.solener.2012.06.017>
- 644 Li, D.H.W., Tsang, E.K.W., Cheung, K.L., Tam, C.O., 2010. An analysis of light-pipe system via full-
645 scale measurements. *Appl. Energy* 87, 799–805. <https://doi.org/10.1016/j.apenergy.2009.09.008>
- 646 Littlefair, P. j., 1990. Review Paper: Innovative daylighting: Review of systems and evaluation methods.
647 *Light. Res. Technol.* 22, 1–17. <https://doi.org/10.1177/096032719002200101>
- 648 Lo Verso, V.R.M., Pellegrino, A., Serra, V., 2011. Light transmission efficiency of daylight guidance
649 systems: An assessment approach based on simulations and measurements in a sun/sky simulator.
650 *Sol. Energy* 85, 2789–2801. <https://doi.org/10.1016/j.solener.2011.08.017>
- 651 Malet-Damour, B., Boyer, H., Guichard, S., Miranville, F., 2017. Performance Testing of Light Pipes in
652 Real Weather Conditions for a Confrontation with Hemera, in: *Journal of Clean Energy*
653 *Technologies. Hong Kong - Chine*, pp. 73–76. <https://doi.org/10.18178/jocet.2017.5.1.347>
- 654 Malet-Damour, B., Guichard, S., Bigot, D., Boyer, H., 2016. Study of tubular daylight guide systems in
655 buildings: Experimentation, modelling and validation. *Energy Build.* 129, 308–321.
656 <https://doi.org/10.1016/j.enbuild.2016.08.019>
- 657 Malet-Damour, B., Guichard, S., Jean, A.P., Miranville, F., Boyer, H., 2018. SHADECO: A low-cost
658 shadow-ring for diffuse measures: State of the art, principles, design and application. *Renew.*
659 *Energy* 117, 71–84. <https://doi.org/https://doi.org/10.1016/j.renene.2017.09.083>
- 660 Maňková, L., Hraška, J., Janák, M., 2009. Simplified Determination of Indoor Daylight Illumination By

- 661 Light Pipes. *Slovak J. Civ. Eng.* 4, 22–30.
- 662 McCluney, R., 2003. Rating of Tubular Daylighting Devices for Visible Transmittance and Solar Heat
663 Gain - Final Report. Cocoa, Florida.
- 664 Miranville, F., 2002. Contribution à l'étude des parois complexes en physique du bâtiment :
665 modélisation, expérimentation et validation expérimental de toitures complexes incluant des
666 produits minces réfléchissants en climat tropical humide. La Réunion.
- 667 Mohelnikova, J., 2009. Tubular light guide evaluation. *Build. Environ.* 44, 2193–2200.
668 <https://doi.org/10.1016/j.buildenv.2009.03.015>
- 669 Nilsson, A.M., Jonsson, J.C., Roos, A., 2014. Spectrophotometric measurements and ray tracing
670 simulations of mirror light pipes to evaluate the color of the transmitted light. *Sol. Energy Mater.*
671 *Sol. Cells* 124, 172–179. <https://doi.org/10.1016/j.solmat.2014.01.049>
- 672 Oakley, G., Riffat, S.B., Shao, L., 2000. Daylight performance of lightpipes. *Sol. Energy* 69, 89–98.
673 [https://doi.org/10.1016/S0038-092X\(00\)00049-9](https://doi.org/10.1016/S0038-092X(00)00049-9)
- 674 Oh, S.J., Chun, W., Riffat, S.B., Jeon, Y. Il, Dutton, S., Han, H.J., 2013. Computational analysis on the
675 enhancement of daylight penetration into dimly lit spaces: Light tube vs. fiber optic dish
676 concentrator. *Build. Environ.* 59, 261–274. <https://doi.org/10.1016/j.buildenv.2012.08.025>
- 677 Samuhatananon, S., Chirarattananon, S., Chirarattananon, S., Chirarattananon, P., 2011. An
678 experimental and analytical study of transmission of daylight through circular light pipes.
679 *LEUKOS - J. Illum. Eng. Soc. North Am.* 7, 203–219.
680 <https://doi.org/10.1080/15502724.2011.10732147>
- 681 Shao, L., Elmualim, A.A., Yohannes, I., 1998. Mirror lightpipes: Daylighting performance in real
682 buildings. *Light. Res. Technol.* 30, 37–44. <https://doi.org/10.1177/096032719803000106>
- 683 Shao, L., Riffat, S.B., Icks, W.H., Yohanne, I.S., 1997. A Study of Performance of Light Pipes Under
684 Cloudy and Sunny Conditions in the UK. *Right Light* 1, 155–159.
- 685 Sharma, L., Ali, S.F., Rakshit, D., 2018. Performance evaluation of a top lighting light-pipe in buildings
686 and estimating energy saving potential. *Energy Build.* 179, 57–72.
687 <https://doi.org/10.1016/j.enbuild.2018.09.022>

- 688 Su, Y., Khan, N., Riffat, S.B., Gareth, O., 2012. Comparative monitoring and data regression of various
689 sized commercial lightpipes. *Energy Build.* 50, 308–314.
690 <https://doi.org/10.1016/j.enbuild.2012.03.053>
- 691 Swift, P.D., 2010. Splayed mirror light pipes. *Sol. Energy* 84, 160–165.
692 <https://doi.org/10.1016/j.solener.2009.10.008>
- 693 Swift, P.D., Smith, G.B., 1995. Cylindrical mirror light pipes. *Sol. Energy Mater. Sol. Cells* 36, 159–
694 168. [https://doi.org/10.1016/0927-0248\(94\)00172-3](https://doi.org/10.1016/0927-0248(94)00172-3)
- 695 Thakkar, V., 2013. Experimental study of Tubular Skylight and comparison with Artificial Lighting of
696 standard ratings. *Int. J. Enhanc. Res. Sci. Technol. Eng.*, 6 2, 4–9.
- 697 Tsang, E.K.W., Kocifaj, M., Li, D.H.W., Kundracik, F., Mohelníková, J., 2018. Straight light pipes'
698 daylighting: A case study for different climatic zones. *Sol. Energy* 170, 56–63.
699 <https://doi.org/10.1016/j.solener.2018.05.042>
- 700 Van Derlofske, J.F., Hough, T.A., 2004. Analytical model of flux propagation in light-pipe systems. *Opt.*
701 *Eng.* 43, 1503. <https://doi.org/10.1117/1.1753272>
- 702 Vasilakopoulou, K., Kolokotsa, D., Santamouris, M., Kousis, I., Asproulas, H., Giannarakis, I., 2017.
703 Analysis of the experimental performance of light pipes. *Energy Build.* 151, 242–249.
704 <https://doi.org/10.1016/j.enbuild.2017.06.061>
- 705 Williams, D., Dorville, J.-F., 2014. Investigating the Thermal and the Lighting Performance of Light
706 Pipes for Sunny and Cloudy Conditions in Insular Tropical Climate. *Electr. Eng.* 2, 221–227.
707 <https://doi.org/10.17265/2328-2223/2014.05>
- 708 Wu, Y., Jin, R., Li, D., Zhang, W., Ma, C., 2008. Experimental investigation of top lighting and side
709 lighting solar light pipes under sunny conditions in winter in Beijing, in: Wang, A., Liao, Y., Song,
710 A., Ishii, Y., Fan, X. (Eds.), 2008 International Conference on Optical Instruments and
711 Technology: Advanced Sensor Technologies and Applications. p. 715710.
712 <https://doi.org/10.1117/12.811992>
- 713 Wu, Y., Li, H., 2012. Experimental study on performance of top lighting solar light pipes in the meeting
714 room in winter in Beijing. *Appl. Mech. Mater.* 178–181, 29–32.

- 715 <https://doi.org/10.4028/www.scientific.net/AMM.178-181.29>
- 716 Wu, Y.P., Wang, X.D., Chen, Z.G., Zhang, C.Y., 2012. Experimental Study on the Influence of
717 Daylighting Performance of Solar Light Pipes by Dusts and Condensation, in: Sustainable
718 Development of Urban Environment and Building Material, Advanced Materials Research. Trans
719 Tech Publications Ltd, pp. 1096–1099. [https://doi.org/10.4028/www.scientific.net/AMR.374-](https://doi.org/10.4028/www.scientific.net/AMR.374-377.1096)
720 [377.1096](https://doi.org/10.4028/www.scientific.net/AMR.374-377.1096)
- 721 Zhang, X., 2002. Daylighting Performance of Tubular Solar Light Pipes: Measurement, Modelling and
722 Validation. Napier University of Edinburgh.
- 723 Zhang, X., Muneer, T., 2000. Mathematical model for the performance of light pipes. *Light. Res.*
724 *Technol.* 32, 141–146. <https://doi.org/10.1177/096032710003200306>
- 725 Zhang, X., Muneer, T., Kubie, J., 2002. A design guide for performance assessment of solar light-pipes.
726 *Light. Res. Technol.* 34, 149–168. <https://doi.org/10.1191/1365782802li041oa>
- 727

