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(71) Applicant: **ISTITUTO NAZIONALE DI ASTROFISICA** [IT/IT]; Viale del Parco Mellini, 84, 00136 ROMA (IT).

(72) Inventors: **GALLI, Paola**; c/o INAF – Osservatorio Astronomico di Brera, Via Bianchi, 46, 23807 MERATE (LC) (IT). **BIANCO, Andrea**; c/o INAF – Osservatorio Astronomico di Brera, Via Bianchi, 46, 23807 MERATE (LC) (IT). **BERTARELLI, Chiara**; c/o POLITECNICO DI MILANO, Dipartimento di Chimica, Materiali ed Ingegneria Chimica, Piazza Leonardo da Vinci, 32, 20133 MILANO (IT). **MORETTI, Paola**; c/o POLITECNICO DI MILANO, Dipartimento di Chimica, Materiali ed Ingegneria Chimica, Piazza Leonardo da Vinci, 32, 20133 MILANO (IT).

(74) Agent: **STUDIO TORTA S.P.A.**; Via Viotti, 9, 10121 TORINO (IT).

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(54) Title: HIGH REFRACTIVE INDEX MONOMERS BASED ON SULFUR AND/OR SELENIUM

(57) Abstract: The invention concerns a high refractive index monomer based on sulfur and/or selenium having general formula (I) and its use in the preparation of polymers, copolymers and photopolymers deriving therefrom through radical ring-opening mechanism.

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"HIGH REFRACTIVE INDEX MONOMERS BASED ON SULFUR AND/OR SELENIUM"

Cross-Reference to Related Applications

This Patent Application claims priority from Italian Patent Application No. 102022000011420 filed on May 30, 2022 the entire disclosure of which is incorporated herein by reference.

Technical Field

The present invention refers to high refractive index monomers based on sulfur and/or selenium having the general specific formula (I) reported below. In addition, the monomers of the present invention are the basis for the development of photopolymers derived therefrom. The invention finds its application forms in all those devices, belonging to different fields of the art, whose optical properties, and specifically the refractive index, strongly depend on the monomers and on the corresponding polymers included in the photoactive materials of said devices. In particular, said photoactive materials represent one of the most sought-after targets thanks to their potential applications in opto-electronics, such as, for example, encapsulated LED and OLED devices, anti-reflective coatings, lenses and holographic optical elements.

With reference to the holographic field, the present

invention lies in the field of high-performance volume (phase) holography with applications ranging from the production of holographic optical elements (diffraction gratings, holographic mirrors or lenses), to the anti-counterfeiting systems, the astronomical instrumentation, the optical memories, the waveguides and up to the wave source sensors.

Background

Among the existing classes of photoactive materials for volume holography, the photopolymers, based on common high refractive index monomers, represent the most promising one since they show a significant modulation of the refractive index when exposed to electromagnetic radiation of appropriate energy. This property is essential to obtain holographic elements with high efficiency. In addition, the photopolymers are characterized by high sensitivity, stability and are achievable with relatively easy processes that do not require hologram chemical development processes.

However, the known photopolymers are not free from defects; first among them, the volume shrinkage during the classic radical polymerizations starting from said common monomers that causes distortions in the photoactive material during the transfer of the holographic pattern. In detail, the volume shrinkage in the photopolymers is due to the

formation of covalent bonds during radical polymerization, characterized by a lower bonding distance than the Van der Waals forces which are instead present between the non-polymerized monomers. In fact, the polymerization of common monomers, such as methacrylates or acrylamides, leads to a volume shrinkage between 14% and 23%.

To resolve the volumetric shrinkage characterizing said known photopolymers, cyclic allylic sulfides (CAS) have been developed since the 1990s. Said CAS monomers polymerize through a radical ring-opening mechanism with consequent limited volume variation between the generated polymers and the constituent monomers, resulting in a volumetric shrinkage due to polymerization of less than 5%. This reduced volumetric shrinkage makes the CAS-based photopolymers particularly interesting for volume holography because, by minimizing the distortions attributable to volumetric shrinkage, they return a hologram with extreme precision without significant deformations.

In view of increasing the refractive index of the CASs, and hence of increasing the modulation of the refractive index of the photoactive materials composed by them in order to extend their applicability based on the different technological needs, the CASs have been functionalized with groups with high polarizability given the known correlation

between refractive index and molecular electronic polarizability: the greater the polarizability of the molecule, the greater the refractive index of the material with the same density.

Functional groups with high polarizability bonded to the CASs include, for example, aryl groups, i.e. aromatic carbocyclic groups having from 6 to 60 carbon atoms.

In this regard, patent application WO 2008/144822 discloses a holographic recording medium comprising a holographic recording layer containing a binder or binder-forming compound, a photopolymerizable recording monomer composition comprising substituted CASs, and a radical photoinitiator. In detail, some substituted CASs have optionally substituted aryl groups, for example with halogens, bonded to the CASs by a sulfur bridge.

Similarly, the article by Evans et al., Adv. Funct. Mater. 2009, 19, 3560-3566, describes a free radical polymerization mechanism for applications in holographic recording media, wherein the monomers involved are substituted and unsubstituted CASs. Precisely, the substituted CAS is (3-methylene-7-(2-naphthalenethio)-1,5-dithiacyclooctane in which naphthalene is bonded to the CAS by sulfur bridge.

However, the modulation of the refractive index of CAS-

based photoactive materials depends not only on the molecular electron polarizability of CASs, but also on the concentration of CASs in the polymer matrix (e.g. PMMA, cab, peg), as a holographic pattern recording medium, in which CASs are generally dispersed. Therefore, in addition to increasing the polarizability of the CASs by means of high polarizability substituents, it is also appropriate to increase the concentration of said substituted CASs with the same polymer matrix, in order to achieve a higher molar refractivity.

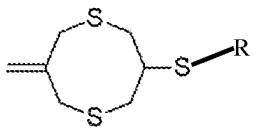
There is therefore the need and the importance to develop new substituted high refractive index CASs which can reach a high concentration with the same polymer matrix and which can therefore advantageously also represent the basis of new photopolymers for applications, for example, in the field of volume holography.

Object of the Invention

It is therefore an aim of the present invention to provide high refractive index monomers capable of having refractive indices comparable to or even higher than known monomers, of ensuring a limited volume variation during polymerization and of achieving a higher molar refraction than the known CASs.

Description of Embodiments

In accordance with this aim, the present invention therefore relates to a high refractive index monomer having general formula (I):



(I)

wherein R represents one or more heteroaryl groups containing at least one heteroatom selected from sulfur or selenium or both and optionally substituted with one or more groups, mutually identical or different, selected from alkyl groups, glycols and/or halogen atoms.

The monomers of the present invention are therefore advantageous in that, the known CASs, here represented by the eight-membered alkyl ring containing an allyl sulfide and a second sulfur atom in meta position with respect to the methylene of the allyl sulfide, is bonded to a high polarizability R group via a sulfur bridge in para position with respect to the methylene of the allyl sulfide, which confers to the monomer having general formula (I) improved chemical-physical properties with respect to the known CASs.

In fact, said high polarizability group R, selected from heteroaryl groups based on sulfur and/or selenium, makes the monomer having general formula (I) intrinsically more

polarizable thanks to the presence of heteroatoms, such as sulfur and/or selenium, in the aromatic system with respect to the known CASs in which the heteroatom, if present, acts as a substituent of the aryl groups.

Thus, a higher molar refraction is obtained starting from a higher molecular polarizability of the CASs according to the invention.

In addition, the monomers of the present invention polymerize through the radical ring-opening mechanism, with consequent formation of polymers characterized by a limited potential volumetric shrinkage in analogy with what is reported in the literature for this type of systems.

The reduced volumetric shrinkage due to polymerization, the increased concentration and the high polarizability, and thus high refractive index, of the functional groups R, make the monomers of the present invention particularly suitable for applications in volume holography.

For the purpose of the present application and of the claims which follow with the term “heteroaryl groups” are meant five- or six-membered aromatic heterocyclic groups, which are single, fused, or linked together by simple bonds (chain configuration in which the heteroaryl groups are repeated from n=1 to n=10, preferably from n=1 to n=6), containing heteroatoms selected from: sulfur, selenium or

both.

Specific examples of single five-membered heteroaryl groups containing a sulfur atom or a selenium atom are thiophene or selenophene.

Further examples of sulfur- and/or selenium-based heteroaryl groups included in the monomer having general formula (I) are:

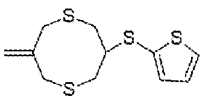
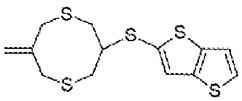
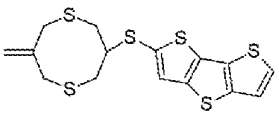
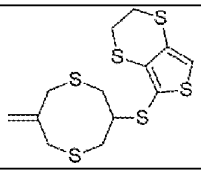
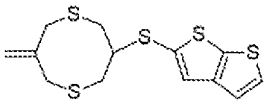
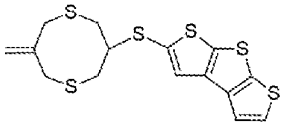
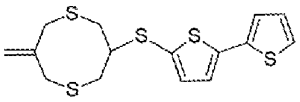
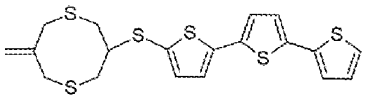
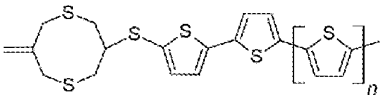
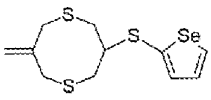
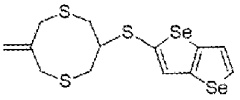
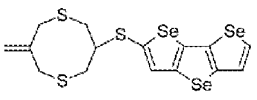
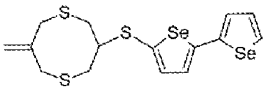
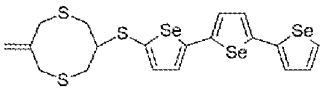
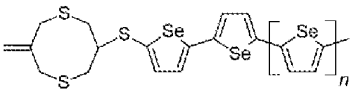
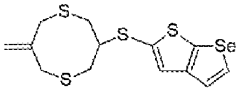
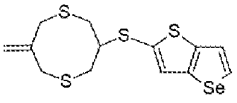
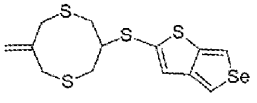
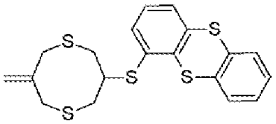
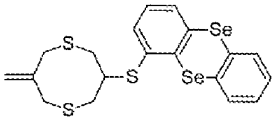
- derivatives of thiophene or selenophene, e.g. bithiophene, terthiophene, biselenophene, terselenophene;
- homo-fused heteroaryl groups comprising two or more five-membered groups or three or more six-membered groups, for example, thieno[2,3-b]thiophene, selenophene[2,3-b] selenophene, selenophene[2,3-b]thiophene, dithieno[2,3-b:2',3'-d]thiophene, dibenzo-1,4-dithiane;
- heteroaryl hetero-fused groups comprising a five-membered group and one or two aryl or heteroaryl six-membered groups, for example thiophene-1,4-dithiane, dibenzothiophene.

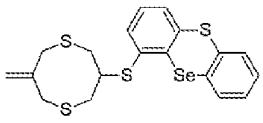
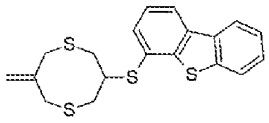
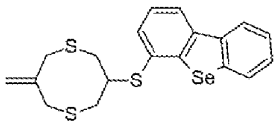
In one embodiment of the invention, the alkyl groups, as substituents of one or more heteroaryl groups of R, contribute to make the monomer having general formula (I) more soluble.

Specific examples of monomers having general formula

(I) useful for the purpose of the present invention are reported in Table 1.

TABLE 1

1		2	
3		4	
5		6	
7		8	
9		10	
11		12	
13		14	
15		16	
17		18	
19		20	

21		22	
23			

The present invention also concerns the use of one or more monomers having general formula (I) for carrying out a polymerization or co-polymerization through radical ring-opening mechanism with consequent formation of a polymer or co-polymer.

The radical ring-opening mechanism, allowed by the monomers having general formula (I), in fact allows to obtain polymers or copolymers characterized by a volumetric shrinkage of less than 5% with application advantages in different sectors of the art including in the field of volume holography.

Co-polymerization may involve different monomers having general formula (I) or may involve at least one monomer having general formula (I) and unsaturated compounds susceptible to radical polymerization. Such unsaturated compounds are for example amides, acrylic esters, dienes, olefins.

The monomer according to the invention may also be employed for carrying out a photopolymerization. According to known techniques, the monomer, dispersed in a polymer matrix (e.g. PMMA, CAB and PEG), is photopolymerized in the

presence of a photoinitiator (e.g. of radical type) and a suitable light radiation.

The monomers of the present invention may form polymers, copolymers or photopolymers having structures and functional groups not otherwise obtainable.

It follows that, said polymers or copolymers or photopolymers retain some properties of their constituent monomers, for example, they have high refractive indices. Therefore, said polymers or copolymers or photopolymers can be advantageously employed for optical applications in which the final properties of the device strongly depend on the refractive index, for example, of the photopolymer comprised therein, like for volume holography.

In order to better understand the present invention and to put it into practice, some illustrative and non-limiting examples thereof are reported below.

Examples

Elemental analysis

NMR Spectrums

The NMR spectra of the synthesized compounds in the following examples were acquired with an NMR spectrometer.

For this purpose, about 1 mg of the sample to be examined was dissolved in 0.4 ml in the deuterated solvent $CDCl_3$ or DMSO-d_6. The scale of the chemical shifts was calibrated with

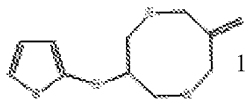
respect to the solvent signal set at 7.26 and 2.50 ppm respectively for the two solvents.

Determination of the refractive index of the synthesized monomers

The refractive index of the synthesized monomers was measured by means of an Abbe refractometer at the wavelength of 589 nm. The proper functioning of the refractometer was verified by measuring the refractive index of some known solvents and by comparing it with the tabulated values.

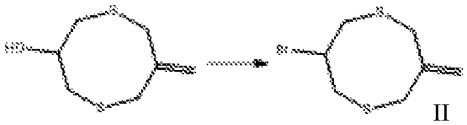
EXAMPLE 1

Synthesis of the monomer 3-methylene-7-(thiophene-2-thiol) -1,5-dithiacyclooctane having formula (1)



1

(1) Synthesis of 3-bromo-7-methylene-1,5-dithiacyclooctane (II)



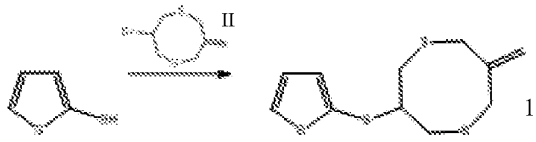
II

PBr_3 (1.02 g) was added dropwise to a cooled solution (0°C) of 7-methylene-1,5-dithiacyclooctan-3-ol (1.0 g) in anhydrous tetrahydrofuran (5 ml) while keeping the solution under stirring and argon atmosphere. The resulting mixture was kept under stirring for a further hour and then a few

drops of water were added to terminate the reaction. The solvent was evaporated using vacuum, the residue was extracted with diethyl ether and subsequently washed with water and dried with sodium sulfate. An equivalent volume of hexane was added to the residue and the resulting mixture was filtered on silica gel. After evaporating the solvent using vacuum, the raw product (0.819 g), corresponding to 3-bromo-7-methylene-1,5-dithiacyclooctane (II) was obtained, which will be used in the following synthesis steps as such without, therefore, requiring a further purification process.

^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 4.84(s, 1H), 4.81 (s, 1H), 3.70-3.08 (m, 9H).

(2) Synthesis of 3-methylene-7-(thiophene-2-thiol)-1,5-dithiacyclooctane (1)



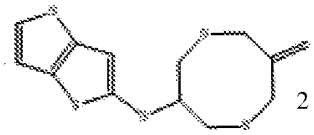
Sodium hydroxide was added to a solution of 2-thiophenethiol (1 mmol) in absolute ethanol (2 mL) under argon atmosphere. The resulting solution was kept under stirring at room temperature and subsequently added to the raw 3-bromo-7-methylene-1,5-dithiacyclooctane (II) (1.1 eq), described above, in absolute ethanol (1.1 mmol in 5 mL). The resulting mixture was kept under stirring overnight at room temperature

and under an inert atmosphere in the dark. Water (20 mL) was added to the mixture to terminate the reaction and the residue was extracted with diethyl ether. The organic phase was washed with water, anhydrified with sodium sulfate and the solvent was removed under vacuum. The product obtained is a brown viscous oil corresponding to 3-methylene-7-(thiophene-2-thiol)-1,5-dithiacyclooctane (1).

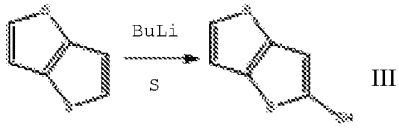
^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.39(1H, dd, J 5.4, 1.2), 7.17 (1 H, dd, J 3.6, 1.2), 7.01 (1 H, dd, J 5.4, 3.6), 4.92 – 4.83 (2 H, m), 3.61 (4 H, dt, J 26.5, 15.7), 3.30 (1 H, dd, J 14.3, 1.5), 3.22 – 3.07 (4 H, m).

EXAMPLE 2

Synthesis of the monomer 3-methylene-7-(thieno(2,3-b)thiophene-5-thiol)-1,5-dithiacyclooctane having formula (2)



(1) Synthesis of thieno(2,3-b)thiophene-5-thiol (III)

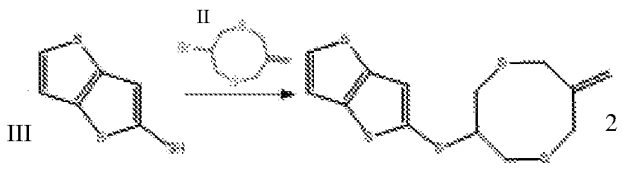


Thieno(2,3-b)thiophene (197 mg, 1 mmol) was dissolved in anhydrous tetrahydrofuran (1 mL) under argon atmosphere, the solution was placed in an acetone bath at -78 °C and

butyllithium (1 eq) was added. The reaction mixture was stirred for 1 hour. Subsequently, sulfur (1 eq) was added and the reaction mixture was kept under stirring for another 2 hours, at the end of which ice water was added to terminate the reaction. Sulfuric acid was added to acidify the resulting mixture, which was subsequently extracted with diethyl ether. The organic phase obtained was anhydrified with sodium sulfate and the residual solvent removed by evaporation: the raw product obtained was purified by elution on chromatographic column (silica gel, petroleum ether), obtaining a pure yellow powdery product, corresponding to thieno(2,3-b)thiophene-5-thiol (III).

^{1}H NMR (400 MHz, DMSO-d_6); δ (ppm) = 7.88(d, J 5.3, 1 H), 7.75 (s, 1 H), 7.49 (d, J 5.3, 1 H).

(2) Synthesis of 3-methylene-7-(thieno(2,3-b)thiophene-5-thiol)-1,5-dithiacyclooctane (2)



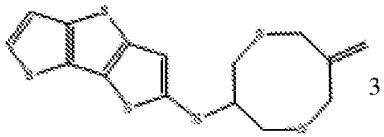
Potassium tertbutoxyde (4.4 eq) was added to a solution of thieno(2,3-b)thiophene-5-thiol (III) (1.1 mmol), synthesized according to the process described above, in anhydrous tetrahydrofuran (2 mL) at room temperature and the mixture was kept under stirring for 30 minutes. Subsequently, 3-bromo-7-methylene-1,5-dithiacyclooctane (II) (0.91 mmol),

synthesized according to the process described in Example 1, was added to the solution keeping it under stirring at room temperature for 20 hours, at the end of which water (20 ml) was added and the mixture was extracted with dichloromethane. The organic phase was washed with water and anhydrified with sodium sulfate. The residual solvent was then evaporated using vacuum obtaining a brown viscous oil corresponding to 3-methylene-7-(thieno(2,3-b)thiophene-5-thiol)-1,5-dithiacyclooctane (2).

^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.39 (d, J=5.0, 2H), 7.28 (s, 1H), 7.27 (d, J=5.0, 2H), 4.91 (d, J=0.8, 1H), 4.88 (s, 1H), 3.66 (m, 6H), 3.35 (d, J=5.6, 1H), 3.23 (m, 2H).

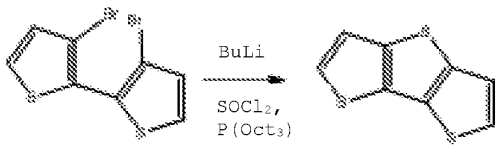
EXAMPLE 3

Synthesis of the monomer 3-methylene-7-(dithieno[3,2-b;2',3'-d]thiophene-2-thiol)-1,5-dithiacyclooctane having formula (3)



3

(1) Synthesis of dithieno[3,2-b:2'3'-d]thiophene (IV)

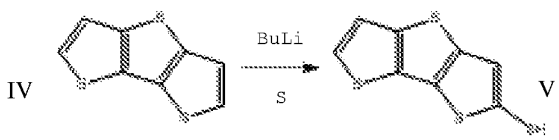


IV

A suspension of 3,3′-dibromo-2,2′-bithiophene (0.50 mmol) in anhydrous diethyl ether and under argon atmosphere was cooled to a temperature of -40°C. n-Butyllithium (2.5 M n-BuLi in hexane, 1.1 mmol) was added to this suspension. The mixture was gradually heated to 0°C and subsequently re-cooled to -78°C. Subsequently, the mixture was stirred at that temperature for 10 minutes and then thionyl chloride (1 eq) was added. The mixture was again gradually heated to room temperature and trioctylphosphine (0.5 mmol) was added. After keeping the mixture under stirring for 3 hours, the reaction was interrupted by adding a saturated solution of sodium bicarbonate and the obtained residue was extracted with chloroform. The organic phase was washed with brine, anhydrified with anhydrous sodium sulfate and concentrated under vacuum. The resulting residue was purified by elution on short chromatographic column of silica gel (dichloromethane) obtaining a yellow solid corresponding to dithieno[3,2-b:2′3′-d]thiophene_(IV).

^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.38 (d, J = 5.1 Hz, 2H), 7.32 (d, J = 5.1 Hz, 2H).

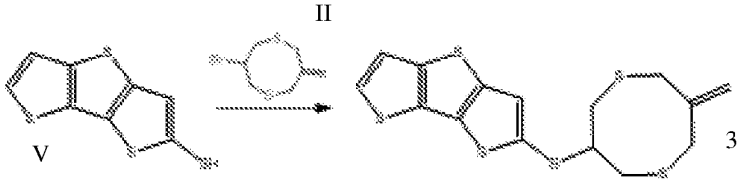
(2) Synthesis of 2-mercaptodithieno[3,2-b;2′,3′-d]thiophene (V)



1 mmol of dithieno[3,2-b:2'3'-d]thiophene (IV), by synthesizing as described above, was dissolved in anhydrous tetrahydrofuran (30 ml) under argon atmosphere. After cooling the solution up to the temperature of -78°C, n-butyllithium (2.5 M n-BuLi in hexane, 1.1 mmol) was added. After 2 hours, sublimated sulfur (1 eq) was added. The reaction mixture was subjected to stirring for 30 minutes at -78°C, then brought to room temperature and hydrolyzed with sodium hydroxide (1 M, 20 mL). Subsequently, the reaction mixture was extracted with dichloromethane and washed with hydrochloric acid (1 M). The collected organic phase was anhydrified with sodium sulfate, filtered and concentrated using vacuum. The raw product obtained was purified by elution on chromatographic column (silica gel, dichloromethane) obtaining a yellow solid corresponding to 2-mercaptodithieno [3,2-b;2',3'-d]thiophene (V).

^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.70 (d, 2 H), 7.52 (d, 2 H), 7.02 (s, 1 H), 3.65 (s, 1H).

(3) Synthesis of 3-methylene-7-(dithieno[3,2-b;2',3'-d]thiophene-2-thiol)-1,5-dithiacyclooctane having formula (3)

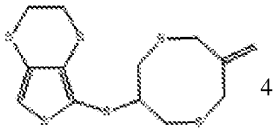


Sodium hydroxide (1 eq) was added to a solution of 2-mercaptodithieno[3,2-b;2',3'-d]thiophene (V) (1 mmol), synthesized as described above, in absolute ethanol (2 ml) under argon atmosphere. The solution was subjected to stirring for 30 minutes at room temperature. Subsequently, the raw 3-bromo-7-methylene-1,5-dithiacyclooctane (II) (0.91 mmol), synthesized according to the process described in Example 1, in absolute ethanol (1.1 mmol in 5 mL), was added to the solution. The reaction mixture is kept under stirring overnight at room temperature and under an inert atmosphere in the dark. Water (20 mL) was added to the mixture to terminate the reaction and the residue was extracted with diethyl ether. The organic phase was washed with water, anhydrified with sodium sulfate and the solvent was removed under vacuum. The product obtained is a brown viscous oil corresponding to 3-methylene-7-(dithieno[3,2-b;2',3'-d]thiophene-2-thiol)-1,5-dithiacyclooctane (3).

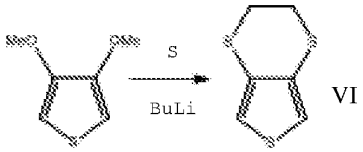
^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.35 (d, J=5.0, 2H), 7.38 (d, J=5.0, 2H), 7.16 (s, 1H), 4.91-4.82 (m, 2H), 3.65-3.57 (m, 4H), 3.30 (m, 1H), 3.19 – 3.047 (m, 4H).

EXAMPLE 4

Synthesis of the monomer 3-methylene-7-(3,4-ethylenedithienothiophene-2-thiol)-1,5-dithiacyclooctane having formula (4)



(1) Synthesis of 3,4-ethylenedithienothiophene (VI)

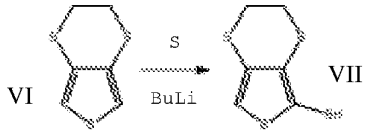


3,4-dimethoxythiophene (1.64 g, 11.37 mmol), p-toluenesulfonic acid (0.04 eq.) and 1,2-ethanedithiol (4 eq.) were dissolved in toluene (10 mL) under stirring under argon atmosphere at 90°C. The reaction was monitored by thin layer chromatography (TLC). After 48 hours, 1,2-ethanedithiol (4 eq.) and p-toluenesulfonic acid (0.04 eq.) were added to the solution kept under stirring for another 24 hours at the same temperature. Subsequently, the reaction mixture was allowed to cool to room temperature and toluene was removed by reducing the pressure. The mixture was extracted with diethyl ether: the organic phase was washed with 5% sodium hydroxide solution and water. The resulting organic phase was anhydrified with sodium sulfate, filtered and concentrated using vacuum. The raw product obtained was purified by elution on chromatographic column (silica gel,

petroleum ether) obtaining a colourless liquid corresponding to 3,4-ethylenedithienothiophene (VI).

^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) = 7.24 (s, 2H), 3.34 (s, 4H).

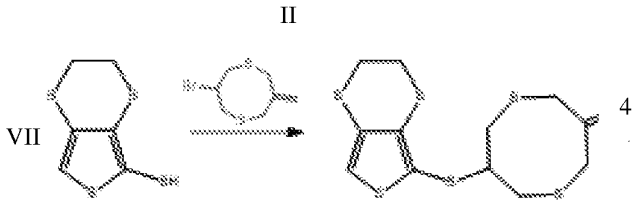
(2) Synthesis of 3,4-ethylenedithienothiophene-2-thiol (VII)



3,4-ethylenedithienothiophene (VI) (350 mg, 2 mmol), synthesized according to the process described above, was dissolved in anhydrous tetrahydrofuran (70 mL). The resulting solution was immersed in an acetone bath at -78°C and butyllithium (1.1 eq.) was added. The reaction mixture is kept under stirring for 1 hour, at the end of which sulfur (1 eq.) is added and kept under stirring for another 2 hours. After 2 hours, the reaction was terminated with the addition of ice water. Sulfuric acid was added to acidify the resulting mixture, which was subsequently extracted with diethyl ether: the organic phase obtained was anhydrified with sodium sulfate and the residual solvent was evaporated, obtaining an orange powdery product corresponding to 3,4-ethylenedithienothiophene-2-thiol (VII).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.05 (s, 1H), 3.24 – 3.20 (m, 2H), 3.12 – 3.09 (m, 2H).

(3) Synthesis of 3-methylene-7-(3,4-ethylenedithienothiophene-2-thiol)-1,5-dithiacyclooctane (4)



Potassium tertbutoxyde was added to a solution of 3,4-ethylenedithienothiophene-2-thiol (VII) (1 mmol), synthesized according to the process described above, in tetrahydrofuran (2 mL) under argon atmosphere under stirring at room temperature for 30 minutes. Subsequently, 3-bromo-7-methylene-1,5-dithiacyclooctane (II) (0.91 mmol), synthesized according to the process described in Example 1, was added to the solution keeping it under stirring at room temperature for a further hour. The reaction mixture is then kept under argon flow for 20 hours in the dark, at the end of which water (20 ml) was added and the mixture was extracted with dichloromethane. The organic phase was washed with water and anhydrified with sodium sulfate. After evaporating the residual solvent using vacuum, an orange viscous oil was obtained, subsequently purified by elution on chromatographic column of pure hexane, hexane/dichloromethane 1/1, pure dichloromethane, obtaining 3-methylene-7- (3,4-ethylenedithienothiophene-2-thiol)-1,5-dithiacyclooctane (4).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 7.34 (s, 2H), 4.90 (s, 1H), 4.85 (s, 1H), 3.60 – 3.16 (13 H, m)

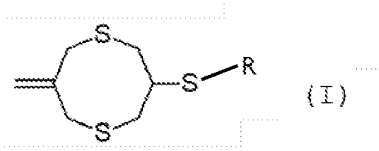
The refractive indices of the monomers (1), (2), (3) and (4) synthesized in Examples 1, 2, 3 and 4 are reported in Table 2:

TABLE 2

Monomer	Refractive index
1	1.645
2	1.645
3	1.619
4	1.592

CLAIMS

1. A high refractive index monomer having general formula (I)



(I)

wherein R represents one or more heteroaryl groups containing at least one heteroatom selected from sulfur or selenium or both and optionally substituted with one or more groups, mutually identical or different, selected from alkyl groups, glycols and/or halogen atoms.

2. A monomer as claimed in claim 1, wherein one or more heteroaryl groups are single, fused or in-chain five-membered rings or six-membered rings.

3. A monomer as claimed in one of the previous claims, wherein a single five-membered heteroaryl group is thiophene or selenophene.

4. A monomer as claimed in one of the previous claims, wherein more in-chain heteroaryl groups are thiophene or selenophene derivatives.

5. Monomer as claim in one of the previous claims, wherein more fused heteroaryl groups are five-membered or six-membered homo-fused rings or hetero-fused rings comprising five-membered or six-membered rings.

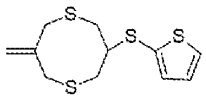
6. Monomer as claimed in claim 5, wherein the five-

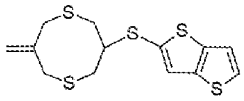
membered homo-fused heteroaryl groups comprise two or more thiophene or two or more selenophene, or combinations thereof.

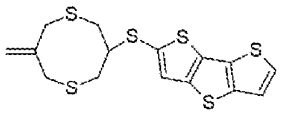
7. Monomer as claimed in claim 5 or 6, wherein the six-membered homo-fused heteroaryl groups comprise a heteroaryl group comprising two heteroatoms selected from sulfur, selenium and combinations thereof and two phenyl groups.

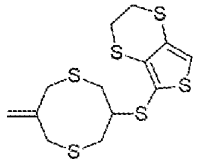
8. Monomer as claimed in one of the claims from 5 to 7, wherein hetero-fused heteroaryl groups comprise at least a five-membered heteroaryl group selected from thiophene or selenophene and one or more aryl groups or six-membered heteroaryl groups selected from phenyl group or dithiane.

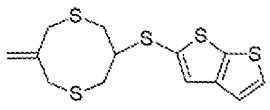
9. Monomer as claimed in one of the previous claims, wherein the monomers having general formula (I) are selected from:

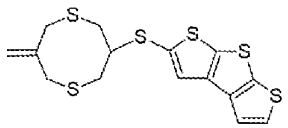
1 

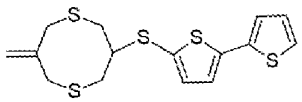
2 

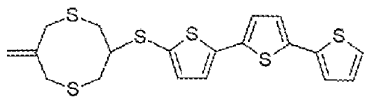
3 

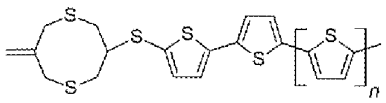
4 

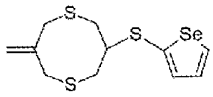
5 

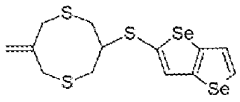
6 

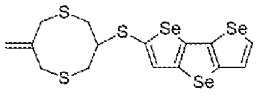
7 

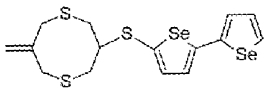
8 

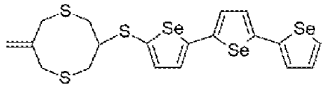
9 

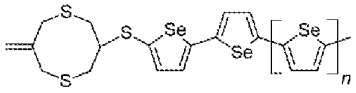
10 

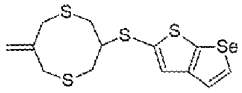
11 

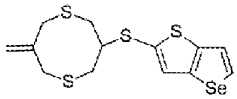
12 

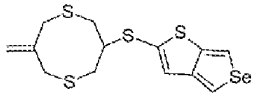
13 

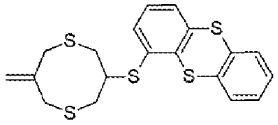
14 

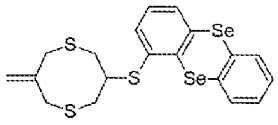
15 

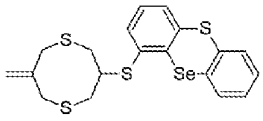
16 

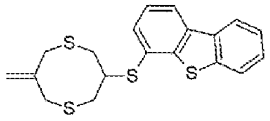
17 

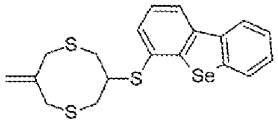
18 

19 

20 

21 

22 

23 

wherein n is an integer number ranging from 1 to 10, preferably from 1 to 6.

10. Use of one or more monomers having general formula (I), as claimed in claims from 1 to 9, for carrying out a polymerization or co-polymerization or photopolymerization through radical ring-opening mechanism.

11. Use of one or more monomers having general formula (I) as claimed in claim 10, wherein the co-polymerization

involves one or more monomers having general formula (I), as claimed in claims from 1 to 9, and an unsaturated compound selected from amides, acrylic esters, dienes, olefins.

12. Use of one or more monomers having general formula (I) as claimed in claim 10, wherein in the photopolymerization the monomers having general formula (I), as claimed in claims from 1 to 9, are dispersed in a polymeric mixture and photopolymerize in the presence of a photoinitiator.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2023/055519

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D409/12 C07D409/14 C07D495/04 C07D495/14 C07F11/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 128 865 A2 (FUJIFILM CORP [JP]) 2 December 2009 (2009-12-02) Whole document, particularly compound M-40 in page 18 and formula II in claim 4.	1-12
A	WO 2008/144822 A1 (ADVANCED POLYMERIK PTY LTD [AU]; EVANS RICHARD ALEXANDER [AU] ET AL.) 4 December 2008 (2008-12-04) cited in the application Whole document, particularly example 6 and claims 9-10	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 September 2023	13/09/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Sahagún Krause, H

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2023/055519

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2128865 A2	02-12-2009	AT 547790 T	15-03-2012
		EP 2128865 A2	02-12-2009
		JP 5236409 B2	17-07-2013
		JP 2010006793 A	14-01-2010
		US 2009297955 A1	03-12-2009
WO 2008144822 A1	04-12-2008	TW 200912515 A	16-03-2009
		WO 2008144822 A1	04-12-2008