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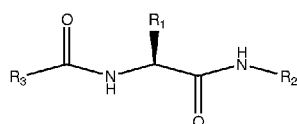
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(54) Title: A FORMULATION, A METHOD OF FORMING THE SAME AND ITS USES THEREOF



(57) Abstract: There is provided a formulation comprising a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6, wherein the organogelator powder comprises a compound of formula (I) as defined herein. There is also provided a method of forming the formulation as defined herein and a method of gelating oil. There is also provided a use of the formulation as defined herein as an oil gelator.

Description

Title of Invention: A Formulation, A Method of Forming The Same And Its Uses Thereof

Technical Field

The present invention generally relates to a formulation and its uses thereof. The present invention also relates to a method of forming the formulation.

Background Art

Oceanic oil spills, which often cause devastating and lasting damages to both environment and ecosystem, are difficult to clean up due to its large area of damage and rough sea conditions. Efficient and cost-effective separation of spilled oil from water body on large scale remains an unsolved challenge to environmental scientists and engineers. Commonly used clean-up techniques such as *in situ* burning, skimmers, booms, solidifiers and sorbents to separate oil from water were not very effective even when applied in combination with other oil-controlling techniques which rely on oil-scavenging bacterial or dispersants. As a result, oil-caused damages and pollutions remained on water bodies for long periods of time.

Recently, phase-selective organogelators (PSOGs) were discovered to exhibit the ability to phase-selectively congeal oil from the surface of the sea water which might possibly enable separation of gelled oil from the water body. Existing PSOGs fall within two categories: solution-based gelators and powder gelators. For solution-based gelators, non-water oil-miscible carrier solvent(s) was required for the dissolution of the gelators, followed by adding the gelator-containing solution into oily water for phase-selective gelation of oil. Gelators of this category were faced with at least two major technical barriers. The first barrier involved the necessity of using toxic or hot carrier solvents, or a large amount of carrier solvent in the solution-based gelator. The other barrier required logistical and technical deployment of volatile and flammable carrier solvents especially on large scale, which is currently the most troublesome hurdle to overcome in real oil spill treatment using solution-based gelators.

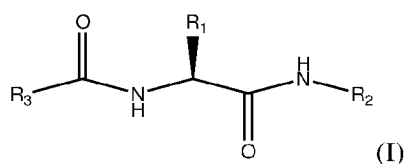
For powder gelators, these were known to produce an extremely slow action in oil gelation during oil spill treatment as a result of their extremely slow dissolution/diffusion speed in oil in the powder form. This slow gelling actions make “on-site” collection of treated oil from the ocean impossible, increased risk of pollution by the oil during and after gelation and further suggested the inability of powder gelators to quickly solidify heavy crude oil of higher viscosities.

There is a need to provide a formulation that overcomes, or at least ameliorates, one or more of the disadvantages described above.

There is also a need to provide a method of gelating oil that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary of Invention

According to a first aspect, there is provided a formulation comprising a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6, wherein said organogelator powder comprises a compound of formula (I):



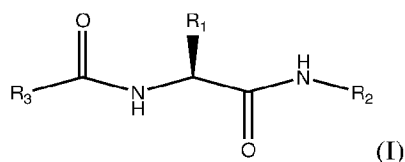
wherein

R_1 , R_2 , and R_3 are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, an optionally substituted C_3 - C_{20} alicyclic group, an optionally substituted C_5 - C_{15} aryl group, an optionally substituted C_6 - C_{30} alkyl-aryl group, an optionally substituted C_3 - C_{20} heterocyclyl group, an optionally substituted C_4 - C_{30} alkyl-heterocyclyl group, an optionally substituted C_5 - C_{15} heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, and an optionally substituted C_5 - C_{15} aryl group.

According to a second aspect, there is provided a method of forming a formulation comprising the steps of:

a) dissolving an organogelator powder in at least one solvent having a relative polarity in the range of 0.3 to 0.6 to form a solution, wherein said organogelator powder comprises a compound of formula (I):



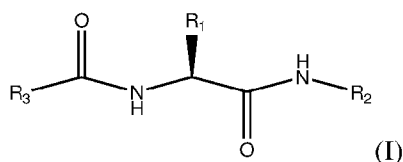
wherein

R_1 , R_2 , and R_3 are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, an optionally substituted C_3 - C_{20} alicyclic group, an optionally substituted C_5 - C_{15} aryl group, an optionally substituted C_6 - C_{30} alkyl-aryl group, an optionally substituted C_3 - C_{20} heterocyclyl group, an optionally substituted C_4 - C_{30} alkyl-heterocyclyl group, an optionally substituted C_5 - C_{15} heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, and an optionally substituted C₅-C₁₅ aryl group; and

b) cooling said solution to obtain the formulation.

According to a third aspect, there is provided a method of gelating oil comprising the step of contacting an oil with a formulation comprising a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6 to form a gelled oil, wherein the organogelator powder comprises a compound of formula (I):

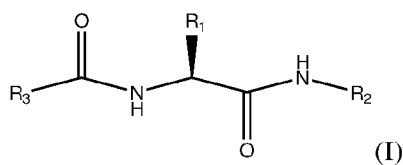


wherein

R₁, R₂, and R₃ are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, an optionally substituted C₃-C₂₀ alicyclic group, an optionally substituted C₅-C₁₅ aryl group, an optionally substituted C₆-C₃₀ alkyl-aryl group, an optionally substituted C₃-C₂₀ heterocyclyl group, an optionally substituted C₄-C₃₀ alkyl-heterocyclyl group, an optionally substituted C₅-C₁₅ heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, and an optionally substituted C₅-C₁₅ aryl group.

According to a fourth aspect, there is provided a use of a formulation comprising a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6 as an oil gelator, wherein said organogelator powder comprises a compound of formula (I):



wherein

R₁, R₂, and R₃ are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, an optionally substituted C₃-C₂₀ alicyclic group, an optionally substituted C₅-C₁₅ aryl group, an optionally substituted C₆-C₃₀ alkyl-aryl group, an optionally substituted C₃-C₂₀

heterocyclyl group, an optionally substituted C₄-C₃₀ alkyl-heterocyclyl group, an optionally substituted C₅-C₁₅ heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, and an optionally substituted C₅-C₁₅ aryl group.

Advantageously, the formulation of the present disclosure may drastically reduce the time taken for the organogelator powder to gel oil. More advantageously, the formulation may achieve rapid full gelation of oils of widely ranging viscosities within minutes at room temperature with powder minimum gelation concentration (PMGC) values, which may translate into significant material cost reductions during an oil spill clean-up.

Further advantageously, the formulation of the present disclosure may remove the necessity of using toxic or a large amount of carrier solvent, thereby improving safety standards during an oil spill clean-up operation and avoiding environmental pollution.

Definitions

The following are some definitions that may be helpful in understanding the description of the present invention. These are intended as general definitions and should in no way limit the scope of the present invention to those terms alone, but are put forth for a better understanding of the following description.

The following words and terms used herein shall have the meaning indicated:

The term "organogelator" as used herein refers to an organic molecule which is capable of gelling oil.

The term "polarity index" or "relative polarity" as used herein refers to the dimensionless Snyder Polarity Index as described by Snyder, L.R. "Classification of the Solvent Properties of Common Liquids" Journal of Chromatography, 92(2): 223-230 (May 1974), and is a relative measure of the degree of interaction of the solvent with various polar test solutes.

The term "minimum gelation concentration" as used herein refers to the minimum concentration of organogelator compound required in an oil or mixture thereof before gelation behaviour may be observed.

The term "powder minimum gelation concentration" as used herein refers to the minimum concentration of organogelator powder required in an oil or mixture thereof before gelation behaviour may be observed.

As used herein, the term "alkyl group" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 20 carbon atoms (e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, etc.). For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-

dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, and the like.

The term “alkenyl group” or “alkene” includes within its meaning monovalent (“alkenyl”) and divalent (“alkenylene”) straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 20 carbon atoms (e.g., 2, 3, 4, 5, 6, 7, 8, 9, etc.) and having at least one double bond, of either *E*, *Z*, *cis* or *trans* stereochemistry where applicable, anywhere in the alkyl chain. Examples of alkenyl groups include but are not limited to ethenyl, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1,3-butadienyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 2-methylpentenyl, 1-heptenyl, 2-heptenyl, 3-heptenyl, 1-octenyl, 1-nonenyl, 1-decenyl, and the like.

The term “alkynyl group” or “alkyne” as used herein includes within its meaning monovalent (“alkynyl”) and divalent (“alkynylene”) straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 20 carbon atoms (e.g., 2, 3, 4, 5, 6, 7, 8, 9, etc.) and having at least one triple bond anywhere in the carbon chain. Examples of alkynyl groups include but are not limited to ethynyl, 1-propynyl, 1-butylnyl, 2-butylnyl, 1-methyl-2-butylnyl, 3-methyl-1-butylnyl, 1-pentylnyl, 1-hexynyl, methylpentylnyl, 1-heptylnyl, 2-heptylnyl, 1-octynyl, 2-octynyl, 1-nonyl, 1-decynyl, and the like.

The term “alicyclic” refers to a group comprising a non-aromatic ring wherein each of the atoms forming the ring is a carbon atom, and may be further classified into monocyclic and polycyclic (e.g., bicyclic and tricyclic) groups. Alicyclic groups may be formed of 3 to 20, or 3 to 12, or 3 to 8, or 3 to 6 carbon atoms, such as three, four, five, six, seven, eight, nine, or more than nine carbon atoms. Alicyclic group may be optionally substituted, i.e. substituted or unsubstituted, and may comprise one or more unsaturated bonds, such as one or more carbon-carbon double bonds. Alicyclics may include cycloalkyls and cycloalkenyls. Examples of alicyclics include, but are not limited to, cyclopropane, cyclobutane, cyclopentane, cyclopentene, cyclopentadiene, cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cycloheptane, and cycloheptene.

The term “heterocyclic” or “heterocyclyl” refers to a saturated, partially unsaturated or fully unsaturated monocyclic, bicyclic or polycyclic ring system containing at least one heteroatom selected from the group consisting of nitrogen, sulfur and oxygen as a ring atom. Examples of heterocyclic moieties include heterocycloalkyl, heterocycloalkenyl and heteroaryl.

The term “heterocycloalkyl” or “alkyl-heterocyclyl” refers to a saturated monocyclic, fused or bridged or spiro polycyclic ring containing at least one heteroatom selected from nitrogen, sulfur, oxygen, preferably from 1 to 3 heteroatoms in at least one ring. Each ring is preferably from 3 to 10 membered, more preferably 4 to 7 membered. Exemplary heterocycloalkyl substituents include pyrrolidinyl, piperidinyl, azepanyl, piperazinyl, dioxanyl, morpholinyl, pyrazolinidyl, morpholinyl, thiomorpholinyl, tetrahydropyridinyl, tetrahydropyrazolopyridine, oxotetrahydroquinolinyl, azabicycloheptanyl,

azabicyclooctanyl, azaspirocyclooctanyl or dioxazaspirodecanyl. A heterocycloalkyl group typically is a C₂-C₁₂ heterocycloalkyl group. A heterocycloalkyl group may comprise 3 to 9 ring atoms. A heterocycloalkyl group may comprise 1 to 3 heteroatoms independently selected from the group consisting of N, O and S. The group may be a terminal group or a bridging group.

The term "aryl" refers to as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C₅₋₇ cycloalkyl or C₅₋₇ cycloalkenyl group are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C₆-C₁₈ aryl group. Exemplary aryls include, but are not limited to, phenyl, naphthyl, indenyl, indanyl, azulenyl, fluorenyl, anthracenyl, furyl, thienyl, pyridyl, pyrrolyl, oxazolyly, thiazolyl, imidazolyl, pyrazolyl, 2-pyrazolynyl, pyrazolidinyl, isoxazolyl, isothiazolyl, 1,2,3-oxadiazolyl, 1,2,3-triazolyl, 1,3,4-thiadiazolyl, pyridazinyl, pyrimidinyl, pyrazinyl, 1,3,5-triazinyl, 1,3,5-trithianyl, indolizynyl, indolyl, isoindolyl, 3H-indolyl, indolynyl, benzo[b]furanyl, 2,3-dihydrobenzofuranyl, benzo[b]thiophenyl, 1H-indazolyl, benzimidazolyl, benzthiazolyl, purinyl, 4H-quinolizynyl, quinolynyl, isoquinolynyl, cinnolynyl, phthalazinyl, quinazolynyl, quinoxalynyl, 1,8-naphthyridinyl, pteridinyl, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, and phenoxazinyl.

The term "alkylaryl" means an alkyl-aryl group in which the aryl and alkyl moieties are as defined herein. Exemplary alkylaryl groups include benzyl, phenethyl, 1-naphthalenemethyl and 2-naphthalenemethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

The term "alkoxyl" as used herein refers to straight chain or branched alkyl-oxy groups. Examples include ethoxy, n-propoxy, isopropoxy, tert-butoxy, and the like.

The term "arylalkoxyl" means an aryl-alkyl-O- group in which the alkyl and aryl are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

The term "alkylamine" or "alkylamino" includes both mono-alkylamino and dialkylamino, unless specified. "Mono-alkylamino" means a Alkyl-NH- group, in which alkyl is as defined herein. "Dialkylamino" means a (alkyl)₂N- group, in which each alkyl may be the same or different and are each as defined herein for alkyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

The term "arylalkylamine" as used herein refers to an amine containing a saturated or unsaturated hydrocarbon chain. A primary arylalkylamine is composed of a ring of 6 to 10 carbon atoms. Exemplary arylalkylamines include but are not limited to phenyl, tolyl, alkoxyphenyl, alkoxycarbonylphenyl, and halophenyl. The term "aryl" as used herein, is phenyl, 1-naphthyl, and 2-naphthyl. The term "substituted aryl" as used herein, is phenyl, 1-

naphthyl and 2-naphthyl having a substituent selected from the group consisting of phenyl, heteroaryl, lower alkyl, lower alkoxy, lower alkylthio, halo, hydroxy, trifluoromethyl, amino, -NH(lower alkyl), and -N(lower alkyl)₂, as well as being mono-, di- and tri-substituted phenyl, 1-naphthyl, and 2-naphthyl containing substituents selected from methyl, methoxy, methylthio, halo, hydroxy, and amino.

The term “alkylcarboxylic acid” refers to a branched or linear alkyl group wherein at least one terminus is substituted with a -COOH group.

The term “arylalkylcarboxylic acid” as used herein refers to an aryl-alkylcarboxylic acid group in which the aryl and alkylcarboxylic acid moieties are as defined herein.

The term “ester” as used herein may refer to compounds having the general formula: R^a-COO-R^b, wherein R^a and R^b denote any organic compound (such as alkyl, aryl, or silyl groups), including those bearing heteroatom containing substituent groups.

The term “carbonyl” refers to moieties possessing an aldehyde (RCHO) or a ketone (RCOR).

The term “ether” refers to a class of organic compounds that contain an oxygen atom connected to two alkyl or aryl groups. They have the general formula R-O-R', where R and R' represent the alkyl or aryl groups. Exemplary ethers include diethyl ether, dimethyl ether, methyl ethyl ether, methyl phenyl ether and polyethylene glycol (PEG). The group may be a bridging group.

The term “alkylether” means an alkyl-O-alkyl group in which the alkyl is as defined herein.

The term “alkylester” means an alkyl-ester-alkyl group in which the alkyl and ester are as defined herein.

The term “alkyletheraryl” means an alkyl-O-aryl or an aryl-O-alkyl group in which the aryl and alkyl are as defined herein.

The term “alkyletheraryl diglycidyl ether” means alkyl-O-aryl diglycidyl ether group or an aryl-O-alkyl diglycidyl ether group in which the aryl and alkyl are as defined herein. Exemplary diglycidyl ethers include 4,4'-isopropylidenediphenol diglycidyl ether.

The term “arylalkylether” means an aryl-alkyl-O- group in which the aryl and alkyl are as defined herein.

The term “optionally substituted” as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one or more groups independently selected from alkyl, alkenyl, alkynyl, thioalkyl, cycloalkyl, cycloalkenyl, heterocycloalkyl, five to six membered optionally benzo-fused heterocycloalkyl having 1 to 3 hetero atoms selected from N, O or S, C₆ or C₁₀-aryl, aryl having 6 to 10 carbon atoms, halo, carboxyl, haloalkyl, haloalkynyl, hydroxyl, alkoxy, thioalkoxy, alkenyloxy, haloalkoxy, haloalkenyloxy, nitro, amino, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroheterocyclyl, alkylamino, dialkylamino, alkenylamine, alkynylamino, acyl, alkenoyl, alkynoyl, acylamino, diacylamino, acyloxy, alkylsulfonyloxy, heterocycloxy, heterocycloamino, haloheterocycloalkyl, alkylsulphenyl, alkylcarbonyloxy, alkylthio, acylthio, phosphorus-containing groups such as phosphono and phosphinyl, aryl, heteroaryl, five to six ring

membered optionally benzo-fused heteroaryl having 1 to 3 hetero atoms selected from N, O or S, alkylaryl, C₁-C₄-alkylaryl having 6 or 10 carbon atoms in the aryl, five to six ring membered optionally benzo-fused C₁-C₆-alkylheteroaryl having 1 to 3 hetero atoms selected from N, O or S, alkylheteroaryl, cyano, cyanate, isocyanate, -C(O)NH(alkyl), and -C(O)N(alkyl)₂, pyrazolyl, imidazolyl, pyrazinyl, piperazinyl or piperidinyl; preferably, when this term is unsubstituted, the functional group may be hydrogen.

The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

Throughout this specification, unless the context requires otherwise, the word “comprise”, or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated step or element or integer or group of steps or elements or integers, but not the exclusion of any other step or element or integer or group of elements or integers. Thus, in the context of this specification, the term “comprising” means “including principally, but not necessarily solely”.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Unless the context requires otherwise or specifically stated to the contrary, integers, steps, or elements of the invention recited herein as singular integers, steps or elements clearly encompass both singular and plural forms of the recited integers, steps or elements.

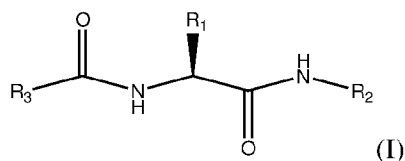
Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations or any two or more of said steps or features.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a formulation will now be disclosed.

The formulation may comprise a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6, wherein said organogelator powder comprises a compound of formula (I):



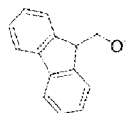
wherein

R_1 , R_2 , and R_3 may be independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, an optionally substituted C_3 - C_{20} alicyclic group, an optionally substituted C_5 - C_{15} aryl group, an optionally substituted C_6 - C_{30} alkyl-aryl group, an optionally substituted C_3 - C_{20} heterocyclyl group, an optionally substituted C_4 - C_{30} alkyl-heterocyclyl group, an optionally substituted C_5 - C_{15} heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

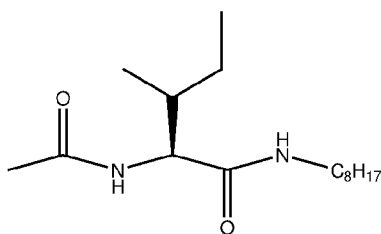
R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, and an optionally substituted C_5 - C_{15} aryl group.

R_1 may be selected from the group consisting of -CH(CH₃)CH₂CH₃, and -(CH₂)₃CH₃.

R_2 may be a linear unsubstituted C_1 - C_{20} alkyl chain. R_2 may be selected from the group consisting of -C₄H₉, -C₆H₁₃, -C₈H₁₇, and -C₁₀H₂₁.

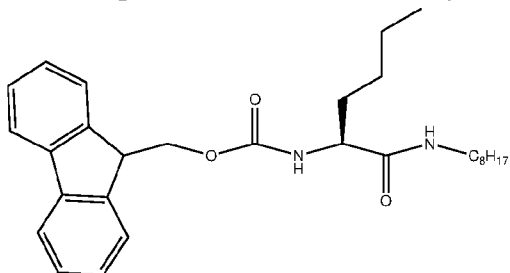


R_3 may be selected from the group consisting of the fluorenylmethyl ether group, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_3 - C_{20} alicyclic group, an optionally substituted C_5 - C_{15} aryl group, an optionally substituted C_6 - C_{30} alkyl-aryl group, an optionally substituted C_3 - C_{20} heterocyclyl group, an optionally substituted C_4 - C_{30} alkyl-heterocyclyl group, and an optionally substituted C_5 - C_{15} heteroaryl group.



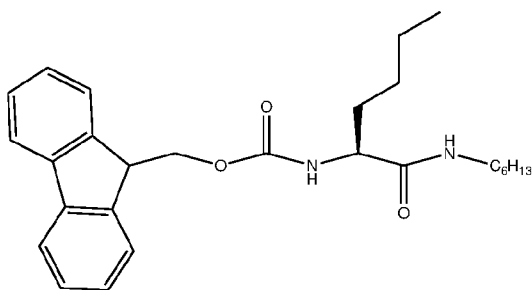
The compound of formula (I) may be

(Ac-Ile-C8),



(F-Leu-C8),

or



(F-Leu-C6).

The solvent may have a relative polarity in the range of about 0.3 to about 0.6, about 0.35 to about 0.6, about 0.4 to about 0.6, about 0.45 to about 0.6, about 0.5 to about 0.6, about 0.55 to about 0.6, about 0.3 to about 0.55, about 0.3 to about 0.5, about 0.3 to about 0.45, about 0.3 to about 0.4, or about 0.3 to about 0.35. The solvent may be a protic or an aprotic solvent. The solvent may be a polar solvent or a non-polar solvent.

The solvent may be selected from the group consisting of acetone (relative polarity of 0.355), acetyl acetone (relative polarity of 0.571), aniline (relative polarity of 0.420), benzonitrile (relative polarity of 0.333), 1-butanol (relative polarity of 0.586), 2-butanol (relative polarity of 0.506), *i*-butanol (relative polarity of 0.552), 2-butanone (relative polarity of 0.327), *t*-butyl alcohol (relative polarity of 0.389), cyclohexanol (relative polarity of 0.509), ethyl acetoacetate (relative polarity of 0.577), 1-heptanol (relative polarity of 0.549), methylene chloride (relative polarity of 0.309), 1-octanol (relative polarity of 0.537), 1-pentanol (relative polarity of 0.568), 2-pentanol (relative polarity of 0.488), 3-pentanol (relative polarity of 0.463), 2-pentanone (relative polarity of 0.321), 2-propanol (relative polarity of 0.546), pyridine (relative polarity of 0.302), dimethylphthalate (relative polarity of 0.309), 1,2-dichloroethane (relative polarity of 0.327), 1-hexanol (relative polarity of 0.559), Dimethylsulfoxide (DMSO) (relative polarity of 0.444), Dimethylformamide (DMF) (relative polarity of 0.386), and acetonitrile (ACN) (relative polarity of 0.460). The formulation may comprise a combination of at least two solvents, wherein each solvent in the combination is as provided above. Advantageously, the use of a combination of solvents may further decrease the gelling time.

The ratio of the compound of formula (I) to the solvent may be about 6:1 to about 1:2, about 5:1 to about 1:2, about 4:1 to about 1:2, about 3:1 to about 1:2, about 2:1 to about

1:2, about 1:1 to about 1:2, about 6:1 to about 1:2, about 6:1 to about 1:1, about 6:1 to about 2:1, about 6:1 to about 3:1, about 6:1 to about 4:1, or about 6:1 to about 5:1.

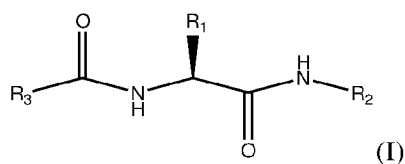
The formulation may be a formulation which is not a dry formulation. The formulation may be in the form of a wet powder or a flocculent powder. Advantageously, the formulation of the present disclosure may achieve significant reductions in reaction time for gelling oil as compared to the gelling time for a dry formulation.

More advantageously, the formulation may achieve powder minimum gelation concentration (PMGC) values of about 10% to about 20% weight per volume for freshly spilled crude oils, about 14% weight per volume for highly weathered light crude oil and about 35% weight per volume for highly weathered heavy crude oil.

Exemplary, non-limiting embodiments of a method of forming a formulation will now be disclosed.

The method of forming a formulation may comprise the steps of:

a) dissolving an organogelator powder in a solvent having a relative polarity in the range of 0.3 to 0.6 to form a solution, wherein said organogelator powder comprises a compound of formula (I):



wherein

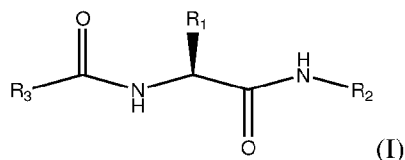
R_1 , R_2 , R_3 , R and R' are as defined herein; and

b) cooling the solution to obtain the formulation.

The organogelator powder may be dissolved by heating in the presence of a polar solvent to form a solution. The solution may be cooled to produce a formulation in the form of a flocculent powder.

Exemplary, non-limiting embodiments of a method of gelating oil will now be disclosed.

The method of gelating oil comprising the step of contacting an oil with a formulation comprising a mixture of an organogelator powder and a solvent having a relative polarity in the range of 0.3 to 0.6 to form a gelled oil, wherein the organogelator powder comprises a compound of formula (I):



wherein

R₁, R₂, R₃, R and R' are as defined herein.

The formulation may be phase selective in that the gelation of oils may take place instantly and selectively in the presence of water or seawater with high capacity at ambient conditions to allow selective separation of the oils from the water or seawater for treatment of oil spills.

The formulation may be contacted with the oil in an amount of about 2 % to about 30 %, about 4 % to about 30 %, about 6 % to about 30 %, about 8 % to about 30 %, about 10 % to about 30 %, about 12 % to about 30 %, about 14 % to about 30 %, about 18 % to about 30 %, about 20 % to about 30 %, about 22 % to about 30 %, about 24 % to about 30 %, about 26 % to about 30 %, about 28 % to about 30 %, about 2 % to about 28 %, about 2 % to about 26 %, about 2 % to about 24 %, about 2 % to about 22 %, about 2 % to about 20 %, about 2 % to about 18 %, about 2 % to about 16 %, about 2 % to about 14 %, about 2 % to about 12 %, about 2 % to about 10 %, about 2 % to about 8 %, about 2 % to about 6 %, or about 2 % to about 4 % by weight per volume of the oil.

The formulation may be contacted with oil in the presence of water, seawater, or wastewater.

After contacting the formulation with the oil, the mixture may be physically agitated.

The oil may be selected from the group consisting of diesel, petrol, crude oil, mineral oil, motor oil, silicone oil, pump oil and natural vegetable oil.

The oil may be below room temperature prior to contacting with the formulation. Room temperature may be a temperature between about 20 °C to about 40 °C, or about 25 °C to about 40 °C, about 30 °C to about 40 °C, about 35 °C to about 40 °C, about 20 °C to about 35 °C, about 20 °C to about 30 °C, or about 20 °C to about 25 °C. Advantageously, the gelation action may be achieved at room temperature without additional heating.

The gelled oil may be in the form of a viscous liquid, a semi-solid, or a solid, and may be collected via a simple filtration and/or reclaimed via a simple reduced pressure or vacuum distillation process.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig.1

[Fig. 1] is a graph representing the gelling time for room-temperature oil gelation of Petrol, Diesel, Grissik and Arab Light by gelator **Ac-Ile-C8** wetted with various solvents at 6% w/v loading with a gelator/solvent wetting ratio of 3:1 (w/w).

Fig.2

[Fig. 2] is a graph depicting the gelator/acetonitrile wetting ratio (w/w) on gelling time for room-temperature oil gelation of Petrol, Diesel, Grissik and Arab Light by **Ac-Ile-C8** in the wet powder form at 6% w/v.

Fig.3

[Fig. 3] is a graph showing the gelling times for gelators with and without wetting at various PMGC values.

Examples

Non-limiting examples of the invention and a comparative example will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1

Gelation Ability Of Powdered Gelator **Ac-Ile-C8** Wetted With Various Types Of Polar Solvents

The gelation ability of powder gelator **Ac-Ile-C8** wetted with various types of polar solvents was investigated. Crude oils (Petrol, Diesel, Weathered Arab light, Weathered Arab heavy, Grissik, Arab Light, Arab Heavy and Ratawi) were selected to represent a majority of the world's actively traded oils, which were obtained from Singapore Refining Co. (SRC) Pte. Ltd. Eight polar solvents were tested with a fixed gelator loading of 6% w/v. The polar solvents are acetic acid (AcOH), Dimethylsulfoxide (DMSO), Dimethylformamide (DMF), ethanol (EtOH), acetonitrile (ACN), ethyl acetate (EA), tetrahydrofuran (THF), dichloromethane (DCM). The gelator was dissolved in each polar solvent by heating, and then cooled to produce solvent-containing gelator in the form of flocculent powder (i.e, in a clump). A spatula was used to scratch the clump to increase its surface area. The wetted gelator was subsequently added to crude oil (Petrol, Diesel, Grissik and Arab light). All gelling times were determined at a shaking speed of 300 rpm using an orbital shaker in the absence of water. In addition, a powdered gelator without wetting with any polar solvent was used as a control. The results of the gelling times in minutes are shown in Tables 1 and 2 and Fig. 1.

Table 1: Solvent effect on gelling time for room-temperature oil gelation by **Ac-Ile-C8** in the powder form with a gelator/solvent wetting ratio of 4:1 (w/w) at gelator loading of 6% w/v.

Oil	Control	AcOH	DMSO	DMF	EtOH	ACN	EA	THF	DCM
Petrol	77	-*	52	54	25	50	66	118	109
Diesel	220	409	309	157	335	92	374	464	197
Grissik	254	-*	126	133	41	76	506	536	380
Arab Light	450	300	166	1140	236	131	323	264	226

*Soluble without gel formation

Table 2: Solvent effect on gelling time for room-temperature oil gelation by **Ac-Ile-C8** in the powder form with a gelator/solvent wetting ratio of 3:1 (w/w) at gelator loading of 6% w/v.

Oil	Control	AcOH	DMSO	DMF	EtOH	ACN	EA	THF	DCM
Petrol	77	-*	59	69	80	35	68	90	115
Diesel	220	427	231	130	-*	84	204	-*	476
Grissik	254	186	89	120	-*	58	221	295	420
Arab Light	450	264	230	540	-*	94	209	-*	226

*Soluble without gel formation

As shown in Table 1 and 2, and Fig. 1, among the tested eight polar solvents and with a fixed gelator loading of 6% w/v, it was surprisingly found that the various solvents were able to reduce the gelling times needed for **Ac-Ile-C8** to gel the various types of oils, with some solvents working better on different types of oils. It was observed that particularly acetonitrile, which is hundreds of times less toxic than crude oil, was the only solvent that consistently and substantially reduced all gelling times needed for **Ac-Ile-C8** to gel four types of oils at both gelator/solvent weight ratios of 4:1 and 3:1. For instance, at weight ratio of 3:1 and loading of 6% w/v, wetting the gelator powder with acetonitrile reduces gelling times significantly by 54, 62, 77 and 79% for Petrol, Diesel, Grissik and Arab Light respectively, as compared to control samples without wetting. On the basis of the fact that these eight solvents had a relative polarity ranging from 0.207 (THF) to 0.654 (EtOH), the use of other solvents with similar polarity (such as those in the range of 0.3 to 0.6) might also lead to good reduction in gelling time not only for **Ac-Ile-C8** but also for other types of powder gelators such as sugar- or fluorenylmethoxycarbonyl (Fmoc)-based powder gelators (i.e., **F-Leu-C6** and **F-Leu-C8**).

Gelation Ability Of Powdered Gelator **Ac-Ile-C8** Wetted With Acetonitrile At Varying Gelator/Solvent Ratios

The gelation ability of powder gelator **Ac-Ile-C8** on crude oils (Petrol, Diesel, Grissik, Arab Light) wetted acetonitrile was investigated at varying gelator/acetonitrile ratios. Similarly, a powdered gelator without wetting with any polar solvent was used as a control. All gelling times were determined at a shaking speed of 300 rpm using an orbital shaker in the absence of water. The results of the gelling times in minutes are shown in Table 3 and Fig. 2.

Table 3: Effect of gelator/acetonitrile wetting ratio (w/w) on gelling time for room-temperature oil gelation by **Ac-Ile-C8** in the powder form at gelator loading of 6% w/v.

Oil	Control	6:1	5:1	4:1	3:1	2:1	1:1	1:2
Petrol	77	58	54	49	35	21	14	17
Diesel	220	110	104	92	84	64	25	55
Grissik	254	112	105	76	58	44	21	26
Arab Light	450	271	169	131	94	68	41	57

As shown in Table 3 and Fig. 2, mixing gelator with solvent in equal weight effects the highest reduction in gelling time for all four oils studied. In particular, gelling times at 6% w/v gelator loading for Grissik and Arab Light at gelator/acetonitrile ratio of 1:1 could be reduced by 92% (from 254 to 21 min) and by 91% (from 450 to 41 min), respectively.

Experiments to compare the gelling times for gelator powder **Ac-Ile-C8** with and without wetting at various PMGC values were conducted for gelator loadings (w/v) of 6% and 10% for

Grissik, 6% and 12% for Arab Light and Arab Heavy, 12% and 20% for Ratawi. The powders were wetted using the same method as disclosed herein. All gelling times were determined at a shaking speed of 300 rpm using an orbital shaker in the absence of water. The results are shown in Fig. 3.

As shown in Fig. 3, it was surprisingly found that application of the optimized wetting conditions to both light (e.g., Grissik and Arab Light) and heavy (e.g., Arab Heavy and Ratawi) crude oils not only established general applicability of the conditions, giving rise to as much as 12 and 105 fold reductions in gelling time for light and heavy crude oils respectively, but also resulted in rapid gelation of these four types of crude oils within minutes with good PMGC values. Additionally, further experiments using the same wetting method as mentioned above was conducted on Weathered Arab Light (WAL) and Weathered Arab Heavy (WAH). As shown in Fig. 3, it was found that highly Weathered Arab Light and Weathered Arab Heavy could also be rapidly gelled within 8 and 10 minutes at gelator loadings of 14 and 35% w/v respectively, and that the times required for Fmoc-based powder gelators, i.e., **F-Leu-C6** and **F-Leu-C8**, to gel Grissik in the powder form at gelator loading of 6% w/v could be similarly shortened from 24 to 2.6 hours for **F-Leu-C6** and from 46 to 1.2 hours for **F-Leu-C8**. This showed that the wetting strategy could be applied to other powder gelators of different structures including sugar-based ones.

Phase-selective Gelation of Grissik and Arab Heavy

Phase-selective gelation of Grissik and Arab Heavy at a larger scale was conducted. In these experiments, 13 mL of crude oil was added onto seawater to prepare an oil slick of 2 mm in thickness, followed by adding wetted gelator **Ac-Ile-C8** into oil at respective loadings of 12% w/v for Grissik and 18% w/v for Arab Heavy at room temperature. Surprisingly, without any mechanical agitation, it merely took 10 and 14 minutes respectively to solidify Grissik and Arab Heavy into floating stiff solids that could be easily strained out using a porous scoop.

Comparative Example

Gelation Ability Of Dry Powder Gelator Ac-Ile-C8 In Various Types Of Crude Oils

The gelation ability of dry powdered gelator Ac-Ile-C8 to gel various types of crude oils was investigated. Dry powdered gelator Ac-Ile-C8 was added at gelator loadings (w/v) of 3.0% to 6.0% for Petrol, Diesel, Grissik, Arab Light, and 4.0% to 12.0% for Arab Heavy and Ratawi. The experiments were conducted with and without shaking. The results of the gelling times are shown in Table 4.

Table 4: Gelling times for various crude oil by dry powder gelator Ac-Ile-C8 at room-temperature.

Crude Oil	Gelator loading (% w/v)	Gelling time without shaking (mins)	Gelling time with shaking (mins)
Petrol	3.0	X	X
	4.0	360	178
	5.0	72	150
	6.0	25	92
Diesel	3.0	X	X
	4.0	X	174
	5.0	X	120
	6.0	1440	95
Grissik	3.0	X	X
	4.0	X	810
	5.0	X	480
	6.0	1320	175
Arab Light	3.0	X	X
	4.0	X	X
	5.0	X	660
	6.0	X	450
Arab Heavy	4.0	X	X
	6.0	X	X
	8.0	X	X
	10.0	X	X
	12.0	X	1440
Ratawi	4.0	X	X
	6.0	X	X
	8.0	X	X
	10.0	X	X
	12.0	X	1560

* "X" means the oil cannot be fully gelled at that percentage of gelator loading

As demonstrated in Table 4, the time taken to gel the crude oils were significantly higher as compared to a wetted powder gelator Ac-Ile-C8. It was also observed that heavier crude oils such as Arab Heavy and Ratawi could not be fully gelled at certain gelator loadings.

The minimum gelation concentration values for dry powdered Ac-Ile-C8 was investigated. Biphasic minimum gelation concentration (BMGC) values were determined by using a biphasic system containing oil on top and water at the bottom. Gelling time for Petrol,

Diesel, Grissik, Arab Light were determined at a gelator loading of 6% w/v. Gelling time for Weathered Arab Light was determined at a gelator loading of 8% w/v. Gelling time for Arab Heavy and Ratawi were determined at a gelator loading of 12% w/v. Gelling time for Weathered Arab Heavy was determined at a gelator loading of 30% w/v. The experimental results are shown in Table 5.

Table 5: BMGC and PMGC values for room-temperature oil gelation by **Ac-Ile-C8**.

Oil	Viscosity (mPa•s, 25 °C)	BMGC (% w/v)	PMGC (% w/v)	Gelling Time (mins)
Petrol	0.4	2.4	2.6	78
Diesel	5.2	2.4	2.9	222
Grissik	0.7	1.8	3.9	252
Arab Light	2.7	2.2	5.0	450
Weathered Arab Light	11.1	2.6	7.7	1380
Arab Heavy	42.5	3.5	12	1440
Weathered Arab Heavy	294.4	5.9	29	1260
Ratawi	81.9	3.8	16.2	1560

As demonstrated in Table 5, powder minimum gelation concentration (PMGC) values were determined with a gelling time fixed to 24 hours for eight oils including two weathered oils. It was observed that the PMGC values varied from 2.6 to 29% w/v, and gelling times at gelator loadings of 6 to 30% w/v fall within 78 to 1560 minutes (1.3 to 26 hours). The time taken for **Ac-Ile-C8** to gel crude oils with reasonable PMGC values was too long, rendering it practically not useful.

Industrial Applicability

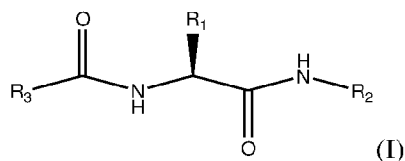
The formulation of the present disclosure may be applied in oil spill clean-up operations, or remedy damages caused by oil pollution in wastewater passages, reservoirs, or other water bodies.

The formulation of the present disclosure may also be applied as a household remedy for removing oil or grease.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A formulation comprising a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6, wherein said organogelator powder comprises a compound of formula (I):



wherein

R_1 , R_2 , and R_3 are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, an optionally substituted C_3 - C_{20} alicyclic group, an optionally substituted C_5 - C_{15} aryl group, an optionally substituted C_6 - C_{30} alkyl-aryl group, an optionally substituted C_3 - C_{20} heterocyclyl group, an optionally substituted C_4 - C_{30} alkyl-heterocyclyl group, an optionally substituted C_5 - C_{15} heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, and an optionally substituted C_5 - C_{15} aryl group.

2. The formulation of claim 1, wherein the solvent is selected from the group consisting of acetone, acetyl acetone, aniline, benzonitrile, 1-butanol, 2-butanol, *i*-butanol, 2-butanone, *t*-butyl alcohol, cyclohexanol, ethyl acetoacetate, 1-heptanol, methylene chloride, 1-octanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-pentanone, 2-propanol, pyridine, dimethylphthalate, 1,2-dichloroethane, cyclohexanol, 1-hexanol, Dimethylsulfoxide (DMSO), Dimethylformamide (DMF), and acetonitrile (ACN).

3. The formulation of claim 1 or 2, wherein the weight ratio of the compound of formula (I) to the solvent is 6:1 to 1:2.

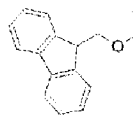
4. The formulation of any one of the preceding claims, wherein R_1 is an optionally substituted C_1 - C_{20} alkyl group.

5. The formulation of any one of the preceding claims, wherein R_1 is selected from the group consisting of -CH(CH₃)CH₂CH₃, and -(CH₂)₃CH₃.

6. The formulation of any one of the preceding claims, wherein R_2 is a linear unsubstituted C_1 - C_{20} alkyl chain.

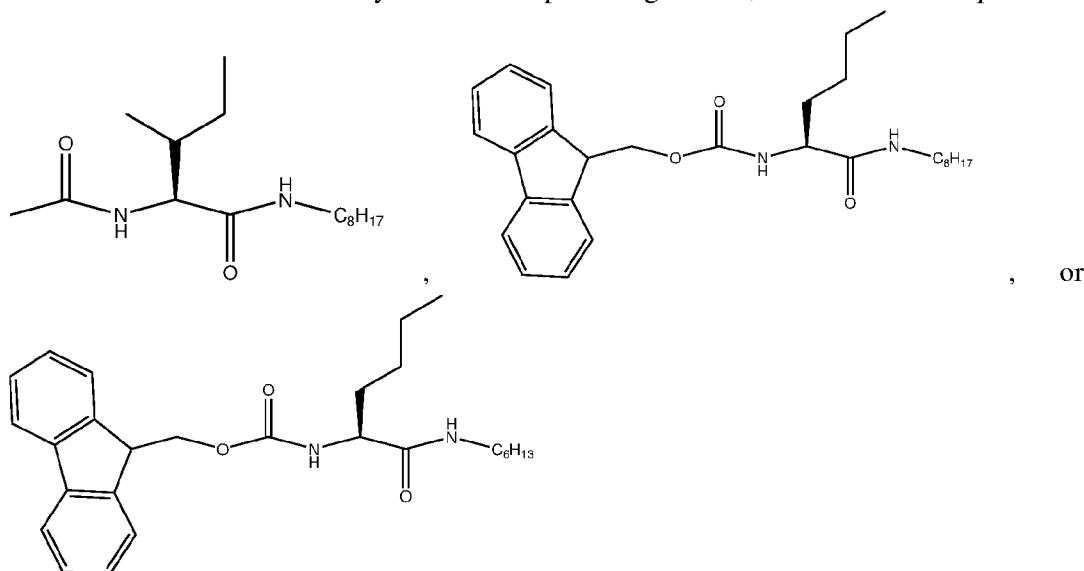
7. The formulation of any one of the preceding claims, wherein R_2 is selected from the group consisting of -C₄H₉, -C₆H₁₃, -C₈H₁₇, and -C₁₀H₂₁.

8. The formulation of any one of the preceding claims, wherein R_3 is selected from the



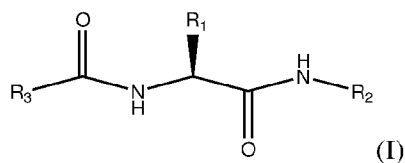
group consisting of , an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_3 - C_{20} alicyclic group, an optionally substituted C_5 - C_{15} aryl group, an optionally substituted C_6 - C_{30} alkyl-aryl group, an optionally substituted C_3 - C_{20} heterocyclyl group, an optionally substituted C_4 - C_{30} alkyl-heterocyclyl group, and an optionally substituted C_5 - C_{15} heteroaryl group.

9. The formulation of any one of the preceding claims, wherein the compound is



10. A method of forming a formulation comprising the steps of:

a) dissolving an organogelator powder in at least one solvent having a relative polarity in the range of 0.3 to 0.6 to form a solution, wherein said organogelator powder comprises a compound of formula (I):



wherein

R_1 , R_2 , and R_3 are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C_1 - C_{20} alkyl group, an optionally substituted C_1 - C_{20} alkoxy group, an optionally substituted C_2 - C_{20} alkenyl group, an optionally substituted C_2 - C_{20} alkynyl group, an optionally substituted C_3 - C_{20} alicyclic group, an optionally substituted C_5 - C_{15} aryl group, an optionally substituted C_6 - C_{30} alkyl-aryl group, an optionally substituted C_3 - C_{20} heterocyclyl group, an optionally substituted C_4 - C_{30} alkyl-heterocyclyl group, an optionally

substituted C₅-C₁₅ heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

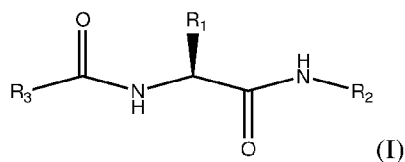
R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, and an optionally substituted C₅-C₁₅ aryl group; and

b) cooling said solution to obtain the formulation.

11. The method of claim 10, wherein the weight ratio of the compound of formula (I) to the solvent is 6:1 to 1:2.

12. The method of claim 10 or 11, wherein the formulation is in the form of a flocculent powder.

13. A method of gelating oil comprising the step of contacting an oil with a formulation comprising a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6 to form a gelled oil, wherein the organogelator powder comprises a compound of formula (I):



wherein

R₁, R₂, and R₃ are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, an optionally substituted C₃-C₂₀ alicyclic group, an optionally substituted C₅-C₁₅ aryl group, an optionally substituted C₆-C₃₀ alkyl-aryl group, an optionally substituted C₃-C₂₀ heterocyclyl group, an optionally substituted C₄-C₃₀ alkyl-heterocyclyl group, an optionally substituted C₅-C₁₅ heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

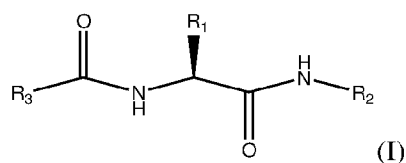
R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, and an optionally substituted C₅-C₁₅ aryl group.

14. The method of claim 13, wherein the formulation is contacted with the oil in an amount of 2 to 30 % by weight per volume of said oil.

15. The method of claim 13 or 14, wherein after contacting the formulation with the oil, the mixture of the formulation and the oil is physically agitated.

16. The method of any one of claims 13 to 15, wherein the formulation is contacted with the oil in the presence of water, seawater, or wastewater.

17. The method of any one of claims 13 to 16, wherein the oil is selected from the group consisting of diesel, petrol, crude oil, mineral oil, motor oil, silicone oil, pump oil and natural vegetable oil.
18. The method of any one of claims 13 to 17, wherein the oil is below room temperature prior to contacting with the formulation.
19. The method of any one of claims 13 to 18, further comprising subjecting the gelled oil to a vacuum distillation process to recover the oil.
20. Use of a formulation comprising a mixture of an organogelator powder and at least one solvent having a relative polarity in the range of 0.3 to 0.6 as an oil gelator, wherein said organogelator powder comprises a compound of formula (I):

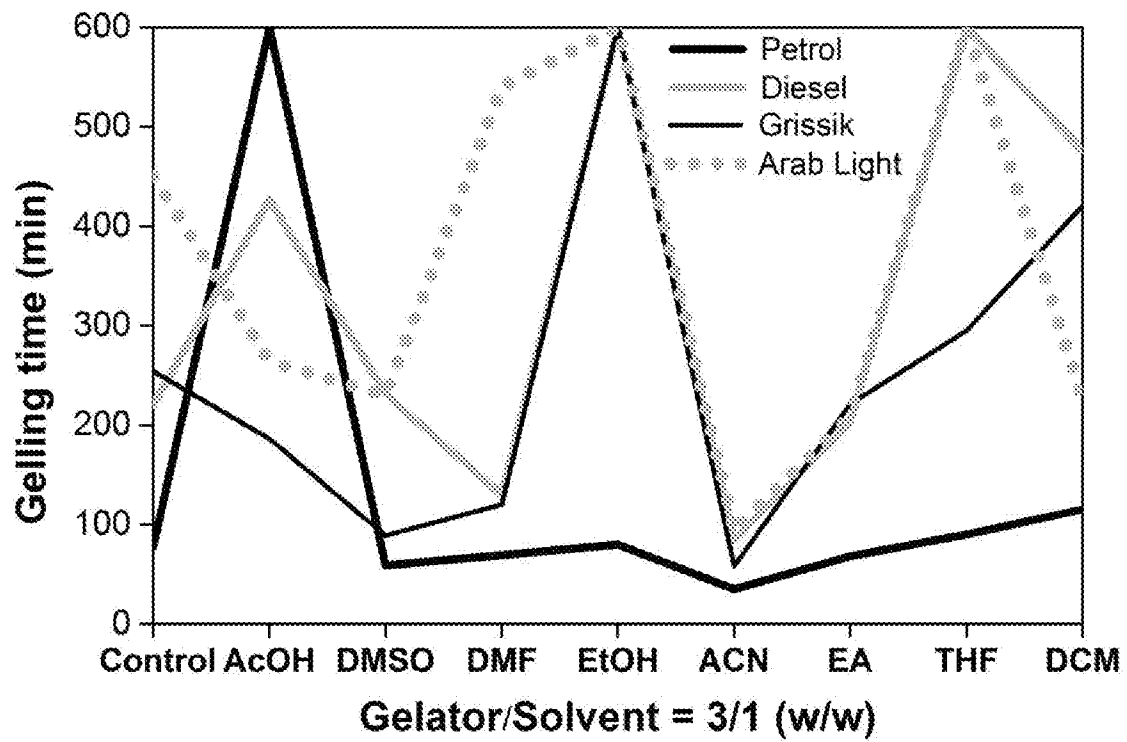


wherein

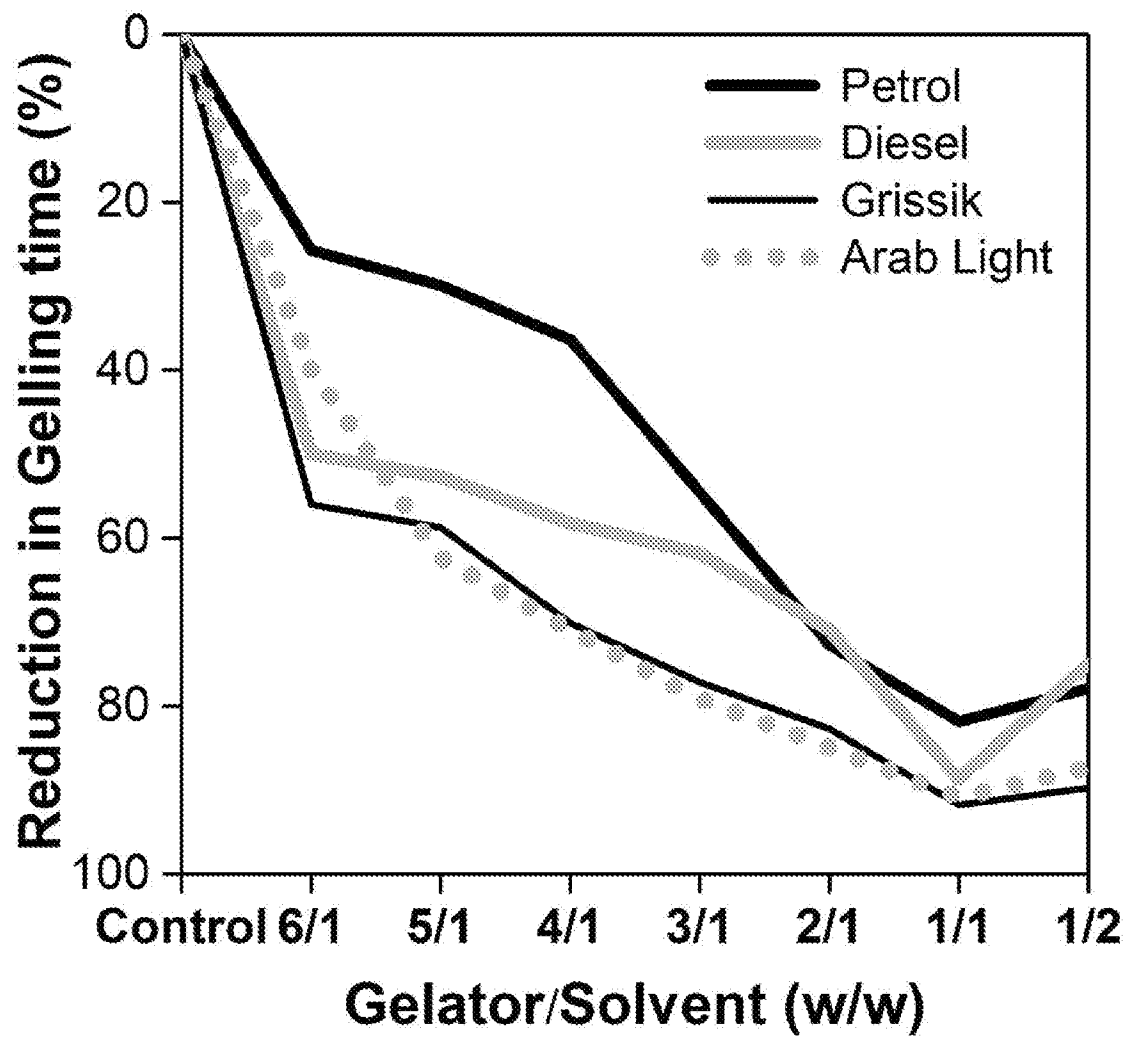
R₁, R₂, and R₃ are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, an optionally substituted C₃-C₂₀ alicyclic group, an optionally substituted C₅-C₁₅ aryl group, an optionally substituted C₆-C₃₀ alkyl-aryl group, an optionally substituted C₃-C₂₀ heterocyclyl group, an optionally substituted C₄-C₃₀ alkyl-heterocyclyl group, an optionally substituted C₅-C₁₅ heteroaryl group, -NRR', -NR, -OR, -SR, -CN, -NO₂, -C(O)-R, -COOR, -R'-C(O)-R, -C(O)-NRR', -C(NR)-R', -SO₂-R, -(SO₂)-OR, -C(S)-R, and -C(S)-RR'; and

R and R' are independently selected from the group consisting of Hydrogen, halogen, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₁-C₂₀ alkoxy group, an optionally substituted C₂-C₂₀ alkenyl group, an optionally substituted C₂-C₂₀ alkynyl group, and an optionally substituted C₅-C₁₅ aryl group.

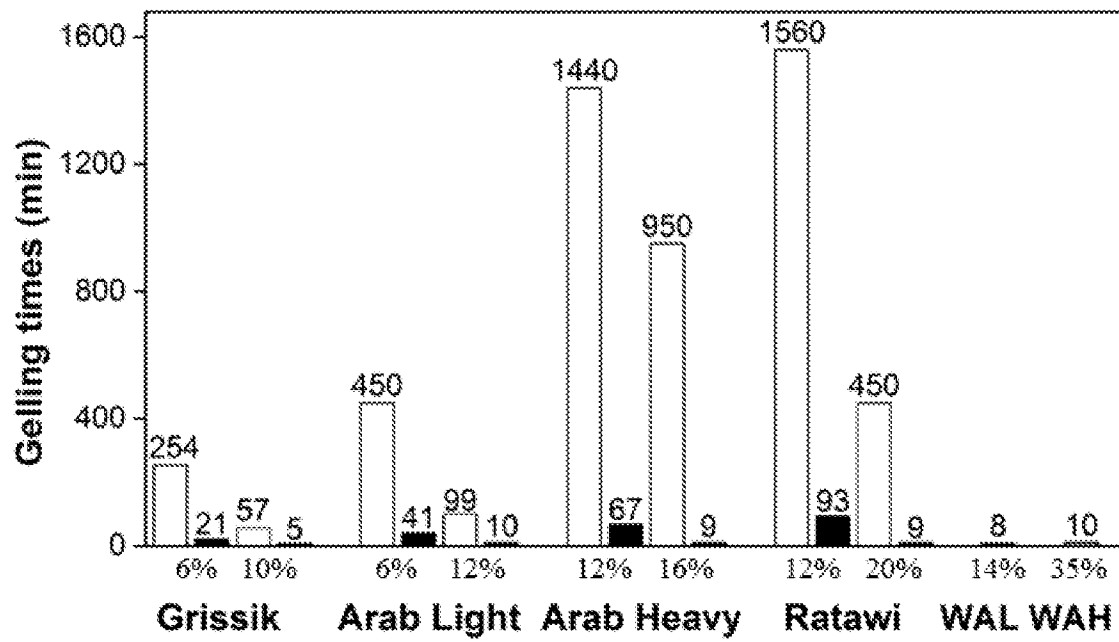
[Fig. 1]



[Fig. 2]



[Fig. 3]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2018/050039

A. CLASSIFICATION OF SUBJECT MATTER

C07C 233/05 (2006.01) C07C 271/22 (2006.01) C08K 5/00 (2006.01) C09K 3/32 (2006.01)

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C, C08K, C07K, C09K

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)

REGISTRY, CAPLUS, EPODOC, WPI: structure search on formula (I), organogelator, gelling, gellant, oil, grease, pollution, spillage, removal, clean up, treatment and related terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	REN, C. ET AL., Instant Room-Temperature Gelation of Crude Oil by Chiral Organogelators. <i>Chemistry of Materials</i> , 10 May 2016, Vol. 28, No. 11, pages 4001-4008 [Retrieved on 2018-04-02] <DOI: 10.1021/ACS.CHEMMATER.6B01367> Page 4004, left-hand column, lines 5 - 17; Figure 1 – F-Ala-C4, F-Ala-C6, F-Leu-C4, F-Leu-C6; Figure 3; Pages S13 – S14; Table S4	1-20
X	SUZUKI, M. ET AL., New low-molecular weight gelators based on L-valine and L-isoleucine with various terminal groups. <i>Tetrahedron Letters</i> , 10 March 2005, Vol. 46, No. 16, pages 2741-2745 [Retrieved on 2018-03-13] <DOI: 10.1016/J.TETLET.2005.02.144> Page 2741, right-hand column, last paragraph; Page 2745, item 10; Scheme 1, Compounds 1a-1c and 2a-2c; Table 1	1-12

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

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

02/04/2018

(day/month/year)

Date of mailing of the international search report

14/04/2018

(day/month/year)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2018/050039

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUZUKI, M. ET AL., Powerful low-molecular-weight gelators based on L-valine and L-isoleucine with various terminal groups. <i>New Journal of Chemistry</i> , 5 June 2006, Vol. 30, No. 8, pages 1184-1191 [Retrieved on 2018-03-13] <DOI: 10.1039/B604847A> Abstract; Page 1188, "Selective organogelation from oil/water"; Page 1191, "Gelation Test"; Scheme 1, Compounds 1-9; Table 1	1-12
X	DEBNATH, S. ET AL., Dipeptide-Based Low-Molecular-Weight Efficient Organogelators and Their Application in Water Purification. <i>Chemistry-A European Journal</i> , 18 July 2008, Vol. 14, No. 23, pages 6870-6881 [Retrieved on 2018-03-13] <DOI: 10.1002/CHEM.200800731> Page 2678, "Selective organogelation from oil/water"; Scheme 3, Compounds 1-9 and 5a – 5h; Table 1	1-9
X	HANABUSA, K. ET AL., Synthesis of Low Molecular Weight Organogelators and Their Physical Gelation. <i>Kobunshi Ronbunshu</i> , 31 December 1998, Vol. 55, No. 10, pages 585-594 [Retrieved on 2018-03-13] <DOI: 10.1295/KORON.55.585> Abstract; Page 586, Section 2.6; Table 3; Scheme 9, Compound 18	1-9
X	US 2005/0199855 A1 (KATO, T. ET AL.) 15 September 2005 [0036], [0085] - [0093]; Reaction scheme (2); Example 4	1-9
P,X	WO 2017/026944 A1 (AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH) 16 February 2017 [0010], [0106], claims 1 and 12	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2018/050039

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005/0199855 A1	15/09/2005	NONE	NONE
WO 2017/026944 A1	16/02/2017	NONE	NONE