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Terminology and the Naming of Conjugates based on Polymers or other Substrates (IUPAC Recommendations 201X)*

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Terminology and the naming of conjugates based on polymers or other substrates (IUPAC Recommendations 201X)+

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Abstract*:* A number of human activities require that certain complex molecules, referred to as active species (drugs, dyes, peptides, proteins, genes, radioactive labels, etc.), be combined with substrates, often a macromolecule, to form temporary or permanent conjugates. The existing IUPAC organic, polymer, and inorganic nomenclature principles can be applied to name such conjugates but it is not always appropriate. These nomenclatures have two major shortcomings: 1) the resulting names are often excessively long and 2) identification of the components (substrate, active species, and link) can be difficult. The new IUPAC naming system elaborates rules for unambiguous and facile naming of any conjugate. This naming system is not intended to replace the existing nomenclature but to provide a suitable alternative when dictated by necessity. Although the rules are intended to be primarily applicable to the naming of polymer conjugates, they are also applicable to naming conjugates with other substrates, which include micelles, particles, minerals, surfaces, pores, etc. The naming system should be used when recognition of the substrate and active substance is essential and will also be useful when constraints of name length make the otherwise preferred IUPAC nomenclatures untenable. The proposed rules for the new naming system are complemented by a glossary of relevant terms.

Keywords: active species, biologically active conjugate, carrier, conjugate, conjugation, drug delivery, pharmacologically active conjugate, protein-based conjugate, substrate, support

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Conj-1 Preamble

In many instances, it is beneficial to permanently or temporarily bind one or several substances, hereafter called the active species, selected for a specific function (color, radioactivity, etc.) or activity (biological, photochemical, etc.), to a substrate [1] used in some cases as a support or a carrier. The result is a new chemical entity referred to as a conjugate, which is designed and engineered to take advantage of combinations of active species and substrates. Although polymeric conjugates dominate in the field, the substrate might be any one of a number of chemical substances such as a molecule, a macromolecule, a micelle, a microparticle, a nanoparticle, or the surface, the pores, or both of a macroscopic organic or inorganic material.

The field of conjugates is rapidly growing and, although nomenclature rules have been well developed by the IUPAC to name inorganic and organic substances, macromolecules, and modified macromolecules [2-5], the corresponding naming principles have major limitations when applied to conjugates because the components cannot be easily recognized and/or, because of their complexity, cannot be simply named using the existing rules.

In covalent conjugate formation, active species and substrates are linked either directly or after suitable chemical modification to provide the means whereby to do so. Such a modification alters the names of the initial components that are no longer recognizable when the current IUPAC nomenclature conventions are applied. In some instances, the connecting or linking fragment plays an important role as it is the case when conjugates include active species that are released by cleavage of the link under predefined physical or chemical conditions. In pharmacology, drugs or other bioactive species such as peptides, proteins, polysaccharides, or polynucleotides are temporarily attached to a carrier for the purpose of being administered locally or transported to a target site in the human body to exert a therapeutic action. In other applications, a conjugate involves molecules such as dyes, radioactive labels, ligands to target receptors present in cell membranes, solubilizing species, and stimuli-responsive entities that comprise smart systems, alone or in combination. Some of these entities are so complex that they are named using abbreviations or acronyms such as FGFa, FGFb, and VEGF growth factors, albumin and fibrinogen proteins, DNA, siRNA, and so on. Therefore, the current IUPAC nomenclature conventions, particularly those of structure-based nomenclature, have obvious limitations when dealing with complex conjugates, either because names are unreasonably long or the identities of the constituents are obscured. The following recommendations provide a more concise system of nomenclature that retains the component names and specifies their connections. In this regard, the nomenclature rules developed by the IUPAC to name modified macromolecules are limited to reflecting chemical modifications only and are thus not suitable.

CONJ-2 Structures and limitations

CONJ-2.1 Structural base conjugation

From a general viewpoint, the structure of a conjugate is composed of one or several constitutional base units referred to as conjugations. The structure of a conjugation is represented schematically in Figure 1, where the arrows represent the functional groups that reacted to form the link.

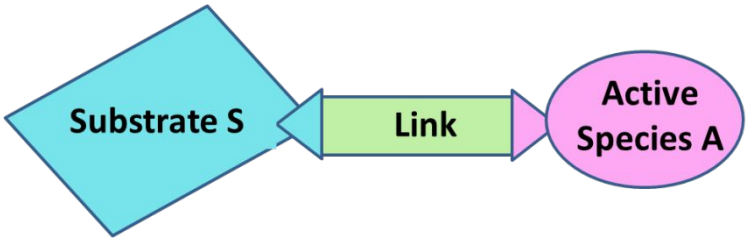

Fig. 1: Schematic representation of a single conjugation comprising a substrate and an active species connected by a link formed from the reaction of the respective functional groups (arrows).

CONJ-2.2 Conjugations in a conjugate

When a conjugate comprises several conjugations, the structure to be named can be as complex as that shown schematically in Figure 2:

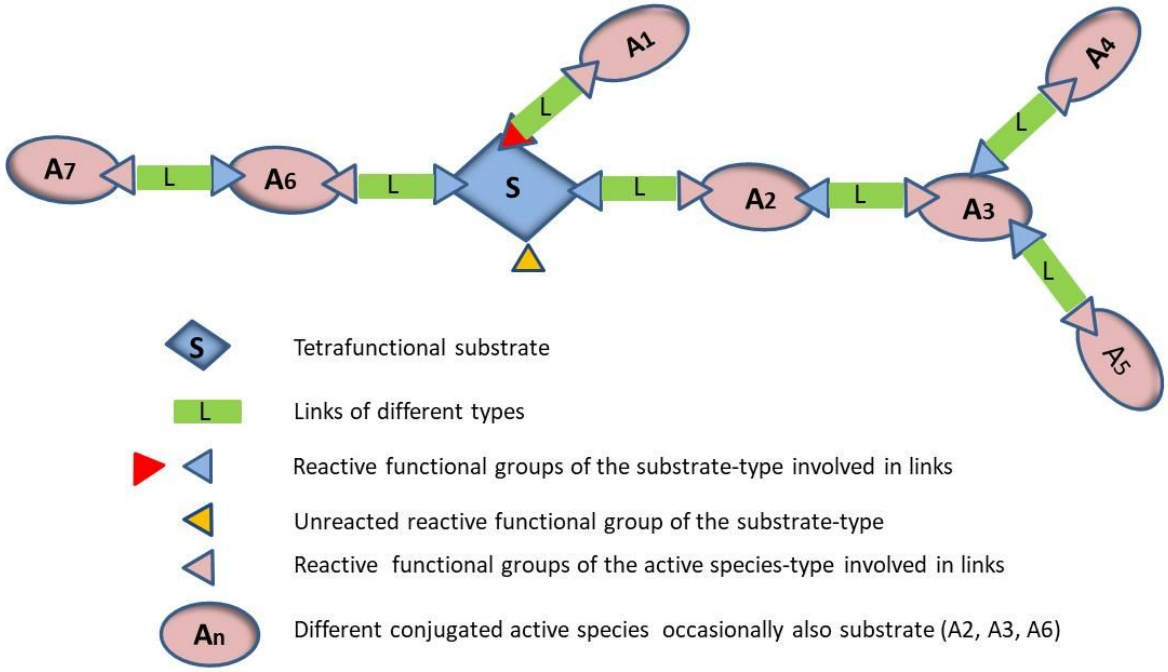

Fig. 2: Schematic representation of hypothetically cumulated single (S-A1 or A3-A5), successive (S-A6-A7), and branched (A3-A4, A3-A5) conjugations that can be found in a conjugate.

In practice, the full name of such a complex must reflect the substrate, the active species, the type of link, and the location of each constituting conjugation.

CONJ-2.3 Complementary structural information

When information on the fraction of reactive functional groups involved in a conjugation is available, and if this information is required, then it is recommended that amount fractions be used, indicated by the italicized symbol *x*, as recommended in [4]. When available, the location of a substrate, an active species, a functional group, and/or a functional group involved in a conjugation or in successive conjugations can be indicated to complement the structural information (*cf*. examples in CONJ-4.2 rule 4 and CONJ-5 cases 2 and 5).

CONJ-2.4 Limitations

Physical adsorption or complexation of a molecule onto a surface cannot be considered as resulting in a conjugate.

In the absence of active species and substrate roles, a chemical compound that results from the reaction or the complexation of two chemical reagents cannot be considered as a conjugate in the present context. Naming such compounds should follow the relevant existing IUPAC nomenclatures.

CONJ-3 Glossary

The following is a list of terms used in this document. Cross references to terms defined elsewhere in this section are denoted in italic typeface.

CONJ-3.1 active species (in IUPAC conjugate terminology)

Molecule with a specific function or activity other than *link* and *substrate* in a *conjugation*.

CONJ-3.2 conjugate (in IUPAC conjugate terminology)

Molecule or compound designed to support, transport, and/or deliver one or several *active species* in order to take advantage of their specificity.

CONJ-3.3 conjugation (in IUPAC conjugate terminology)

Constitutional chemical entity in a conjugate that results from the covalent coupling of an *active species* to a *substrate* with the formation of a *link.*

CONJ-3.4 bioconjugate

Conjugate that involves a *substrate* or an *active species*, or both, that are of biological origin.

CONJ-3.5 carrier (in IUPAC conjugate terminology)

Support in a *conjugate* that allows the transport and the action of one or several active species with or without delivery (modified from Ref. [1]).

CONJ-3.6 link (in IUPAC conjugate terminology)

Constitutive part of a *conjugation* that binds an *active species* to a *substrate*.

Note: When release of the active species is desired, the *link* must be cleavable. (See Ref. [6] for correct naming of the mechanism of cleavage)

CONJ-3.7 prodrug conjugate

Conjugate in which at least one *conjugation* includes a bioactive *active species* to be released by cleavage of the link where its action is desired. (Adapted from Ref. [6]).

CONJ-3.8 spacer

Bifunctional molecule used to form a *spacer arm* in a *conjugation*.

CONJ-3.9 spacer arm

Link used in a *conjugation* to distance the *substrate* from the *active species* that otherwise would have its activity affected by steric or other influences.

CONJ-3.10 substrate (in IUPAC conjugate terminology)

Substance to which an *active species* is covalently linked to form a *conjugation* constitutive of *a conjugate.*

CONJ-3.11 support

Part of a *conjugate* to which one or multiple active *conjugations* linked in series and/or as branches are attached.

Note: Correct use of the terms *support* will infer whether the action of a *conjugate* is expected locally or only after transport away from an initial site, respectively.

CONJ-4 Rules for the naming of conjugates

CONJ-4.1 Basic principles

This document presents an efficient and compact method of conveying standard information about conjugates resulting from one or several conjugations by incorporating within a single conjugate name, an indication of the structure of the conjugate. To this end, a new prefix, **conj***,* an abbreviation of the word “conjugate”, is introduced to specifically begin conjugate names, and a new connective, *link*, is introduced to indicate the conjugation by bonding of an active species to a substrate. The name of each conjugation includes the chemical name of the link, the names of the substrate and the active species, and the relevant functional groups on the substrate and the active species involved in the link formation.

The new method to name conjugates is to be known as the IUPAC conjugate naming mode, while the names are conjugate names. It is applicable to any kind of substrate (be it a molecule, a macromolecule, an organic or inorganic solid or particle, a micelle, or an aggregate of self-assembled molecules, etc.) and to all kinds of active species.

The goal of this new naming mode is to allow easy recognition of the substrate S and of the active species A involved in each conjugation that formed a conjugate. Approved IUPAC names, traditional names, and source-based names can be used for substrates [4] and international non-proprietary names [7] for active species. The use of proprietary names is excluded. Structure-based names are not explicitly excluded but, in practice, substrates and

active species cannot be easily recognized because of complexity or because their structures are unknown, too complex (proteins), variable (DNA), or beyond the conventions of IUPAC nomenclature (minerals).

CONJ-4.2 Rules

Rule 1: The IUPAC name of a conjugate is composed of the prefix "conj" complemented by the name appended in parentheses and constructed by application of a basis of naming to each constituting conjugation successively, using the established nesting order {[({[(...)]})]} for multiple enclosing marks recommended by the IUPAC [4] combined with commas or semicolons according to the role of the conjugations in the conjugate (see rules 2 and 3).

The basis of naming is:

$$[S, (F_S)]\text{-}\textit{link}(F_S \leftrightarrow F_A)\text{-}[(z_{Fs}), (F_A), A]$$

where S is a substrate having one of its *m* reactive functional groups named Fs engaged in a constitutive conjugation; A is an active species having one of its *n* reactive functional groups named F_A bound to S; ($F_S \leftrightarrow F_A$) is the chemical representation of the link, established by reaction between F_S and F_A; and (z_{Fs}) is the amount fraction of F_s involved in the (F_S + F_A) link appended in parentheses and separated by a comma from the [(F_A), A] part specific to the bound active species A.

Note 1: When the amount fraction of Fs is unknown or not necessary, the part in the conjugation name specific to the active species is limited to [(FA), A].

Note 2: When the monofunctional substrate, support or carrier, is a macromolecule, the amount of fraction (z_{Fs}) may correspond to the amounts of mole fraction of the various constitutional repeating units (a:b:c… *x*).

Note 3: In the case of a macromolecular conjugate, the name of the conjugate is unique regardless of whether the conjugate was obtained by polymerization, copolymerization, polycondensation, chemical modification, or a combination of these.

Example:

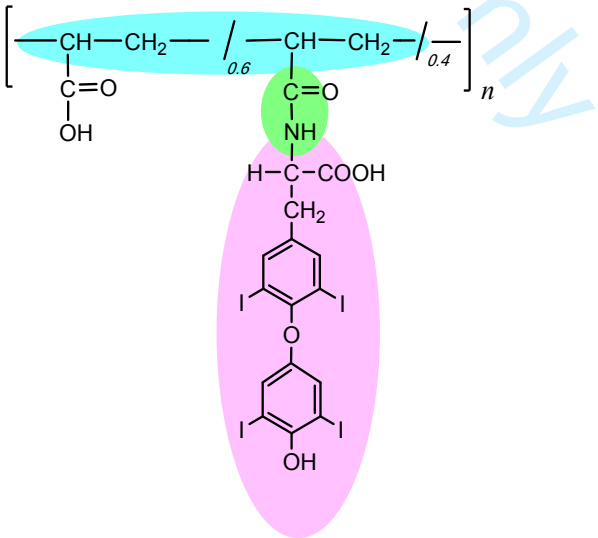

Fig. 3: Hypothetical conjugate composed of poly(acrylic acid) (*m* = 1) as the substrate conjugated with thyroxine (*n* = 1) as the active species, with 40 % of the acrylic carboxyl groups being involved in the conjugation.

IUPAC structure-based name:
poly[(1-carboxyethylene)/[1-({1-carboxy-2-[4-(4-hydroxy-3,5-diiodophenoxy)-3,5-diiodophenyl]ethyl}carbamoyl)ethylene] (0.6:0.4 *x*)

IUPAC source-based name:
poly[(acrylic acid)-*co*-(*N*-acryolylthyroxine)](0.6:0.4 *x*)

IUPAC chemical-modification name:
poly[(acrylic acid)-*mod*-(*N*-acryloylthyroxine)] (*x* = 0.4)

IUPAC conjugate name:
conj{[poly(acrylic acid), (COOH)]-*link*(-CO-NH-)-[(0.4), (NH_2), thyroxine]}

Rule 2: When different active species Ai are conjugated to a monofunctional substrate S (*m* = 1) via the same F_A functional group, the first part of the basis of naming is applied once as [S, (F_S)]-*link*(F_S ↔ F_A)- followed by the [(z_{Fs}), (F_A), A] part of the basis of naming specific to each Ai separated by a comma.

Example:

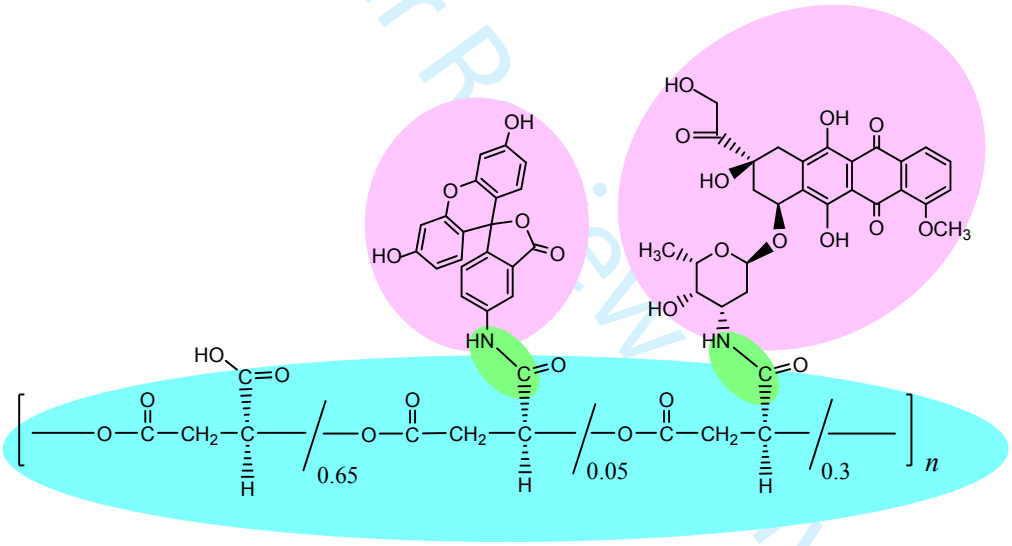

Fig. 4: Conjugate between a chiral polyelectrolyte, poly[(*S*)-β-malic acid], (*m* = 1), labelled with a dye (5-aminofluorescein) and conjugated with a drug (doxorubicin), both active species being bound by an amide link; the amount fractions of COOH linked to the dye and the drug are (0.05) and (0.3), respectively. The amount fraction of the remaining carboxylic functions is easily deduced as (0.65). The active species in the conjugate name are listed in alphabetical order, a non-mandatory ordering.

IUPAC structure-based name:
poly({oxy[(3*S*)-3-carboxy-1-oxopropane-1,3-diyl]}/(oxy{(3*S*)-3-[(3',6'-dihydroxy-3-oxo-3*H*-spiro[[2]benzofuran-1,9'-xanthen]-5-yl)carbamoyl]-1-oxopropane-1,3-diyl)/{oxy[(3*S*)-3-{[(2*S*,3*S*,4*S*,6*R*)-3-hydroxy-2-methyl-6-{[(1*S*,3*S*)-3,5,12-trihydroxy-3-(hydroxyacetyl)-10-methoxy-6,11-dioxo-1,2,3,4,6,11-hexahydrotetracen-1-yl]oxy}oxan-4-yl]carbamoyl}-1-oxopropane-1,3-diyl]}) (0.65:0.05:0.3 *x*)

IUPAC conjugate name:
conj({poly[(*S*)-β-malic acid], (COOH)}-*link*(-CO-NH-)-[(0,05), (NH_2), 5-aminofluorescein)], [(0.3), (NH_2), doxorubicin])

Rule 3: When several active species Ai bearing only one reactive functional group F_{Ai}, in which each are bound to a multifunctional substrate, (m > 1), semi-colons are used to separate the basis of naming applied to each (F_{Sm})-based conjugation or successive series of conjugations appended in suitable enclosing marks.

Example:

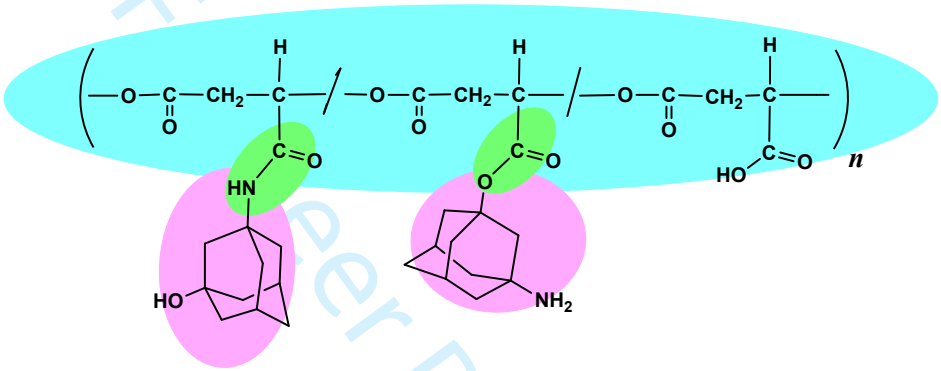

Fig. 5: Conjugate synthesized by reaction of poly[(*RS*)-malic anhydride)] with 3-amino-1-adamantanol (n = 2) to yield a conjugate with two types of links (amide and ester) localized in alphabetical order, the substrate being poly[(*RS*)-malic acid)] at the end (unknown quantitative composition and unit distribution).

IUPAC structure-based name:
poly{(oxy{3-[(3-hydroxyadamantan-1-yl)carbamoyl]-1-oxopropane-1,3-diyl})/[oxy(3-{[(3-aminoadamantan-1-yl)oxy]carbonyl}-1-oxopropane-1,3-diyl)]/[oxy(3-carboxy-1-oxopropane-1,3-diyl)]}

IUPAC conjugate name:
conj({poly[(*RS*)-β-malic acid], (COOH)}-*link*(-CO-NH-)-[(NH_2), 3-aminoadamantan-1-ol]; {poly[(*RS*)-malic acid], (COOH)}-*link*(-CO-O-)-[(OH), 3-aminoadamantan-1-ol])

Note: In the absence of ordering imposed by the synthesis protocol, the links of the conjugations directly attached to the support are preferably ordered alphabetically, amide before ester in this example.

Rule 4: When the functional groups (F_{A1}) and (F_{A2}) of a bifunctional active species are engaged in upstream and downstream conjugations, respectively, the functional group that is engaged in the downstream conjugation is indicated after the name of the active species as [(z_{Fs}), (F_{A1}), A, (F_{A2})], meaning that A is now considered as a substrate for the downstream conjugation.

Example:

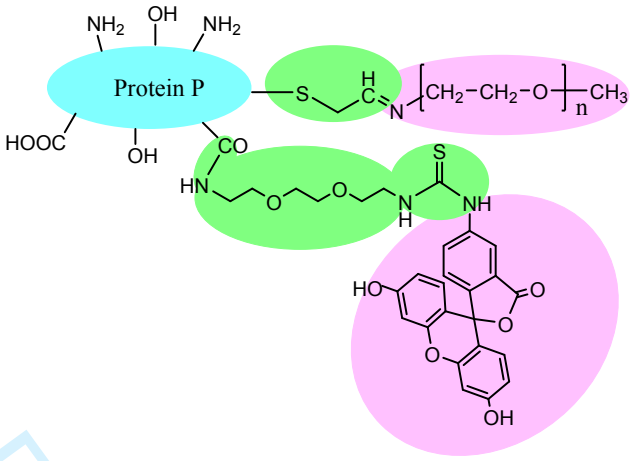

Fig. 6: Hypothetical conjugate of a multifunctional protein conjugated to (α-methyl-ω-aminopolyoxirane) and further modified using a link derived from iodoacetaldehyde, and a fluorescent label derived from fluorescein isothiocyanate coupled using ethylene glycol bis(2-aminoethyl) ether as the spacer. The location of Fs_i of the protein is indicated.

IUPAC conjugate name:

conj({[protein P, $(COOH)_{Asp35}$]-*link*(-CO-NH-)-[(NH_2), ethylene glycol bis(2-aminoethyl) ether, (NH_2)]-*link*(-NH-CS-NH-)-[(S=C=N), fluorescein 5-isothiocyanate]}; {[protein P, $(SH)_{Cys123}$]-*link*(-S-CH_2-CH=N-)-[(1), (NH_2), α-methyl-ω-aminopoly(oxirane)]})

Note 1: In this example, there are three different links represented by their chemical structure, (-CO-NH-), (-S-CH_2-C=N-), and (-NH-CS-NH-), and one spacer arm.

Note 2: The location of the amino acid residues bearing the reactive COOH and NH_2 functional groups present in the multifunctional protein is indicated as the subscript.

CONJ-5 Examples of conjugate naming

Case 1:

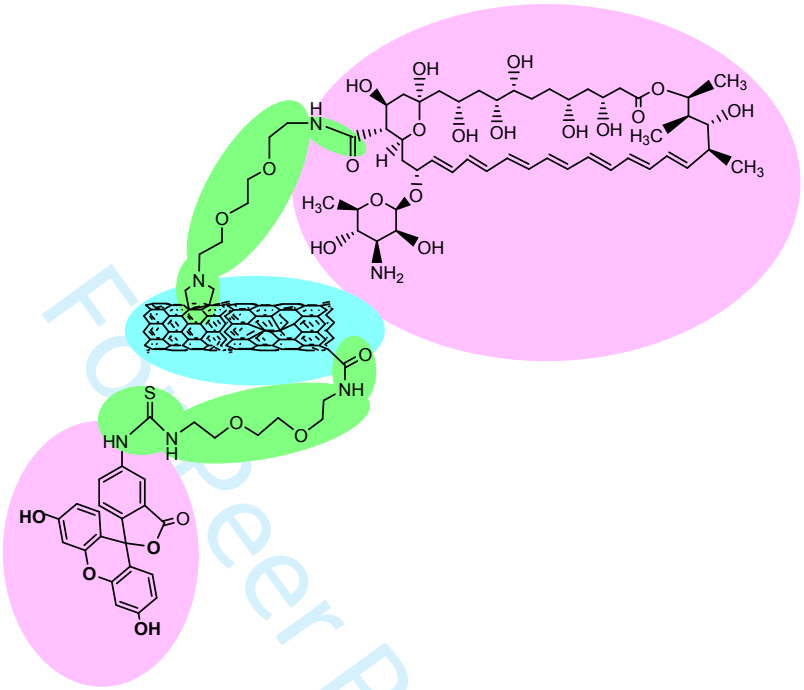

Fig. 7: Conjugate of oxidized single-wall carbon nanotubes with fluorescein isothiocyanate and then amphotericin B using ethylene glycol bis-(2-aminoethyl) ether as the spacer [8].

IUPAC conjugate name:

conj({[(oxidized SWCNT), (COOH)]-*link*(-CO-NH-)-[(NH_2), ethylene glycol bis(2-aminoethyl) ether, (NH_2)]-*link*(-NH-C(=S)-NH-)-[(S=C=N), fluorescein 5-isothiocyanate]}; {[(oxidized SWCNT), (C=C)]-*link*-(-CH_2-N-CH_2-)-[(NH_2), ethylene glycol bis(2-aminoethyl) ether, (NH_2)]-*link*(amide)-[(COOH) amphotericin B]})

Case 2:

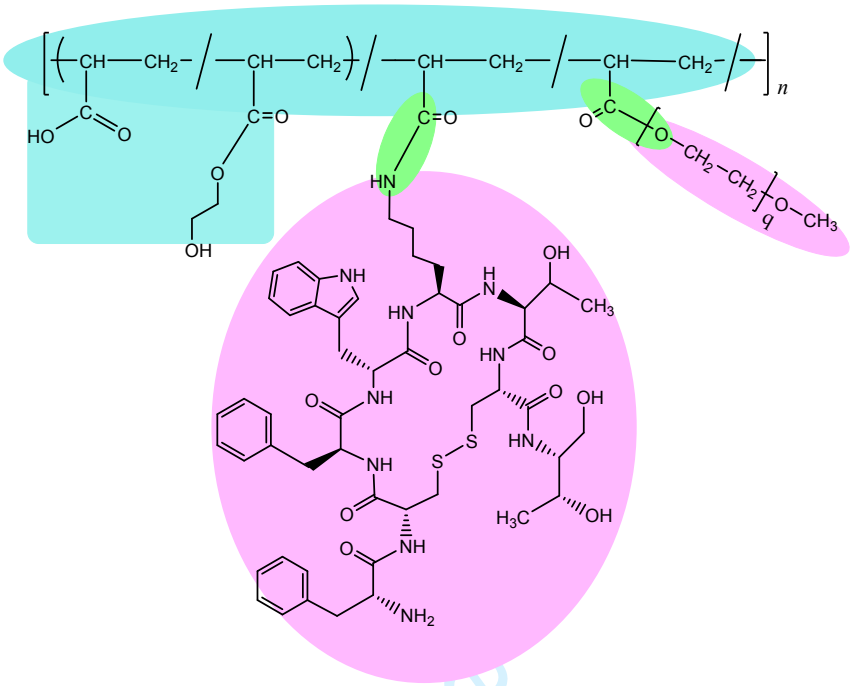

Fig. 8: Conjugate resulting from successive partial couplings of α-hydro-ω-methoxypoly(oxyethylene) (solubilizing entity) and the octreotide peptide to a poly(acrylic acid)-co-(2-hydroxyethyl acrylate) copolymer in the absence of known composition and unit distribution.

IUPAC conjugate name:

conj({[poly(acrylic acid)-*co*-(2-hydroxyethyl acrylate), (COOH)]-*link*(-CO-O-)-[(OH), α-hydro-ω-methoxypoly(oxyethylene)]}; {[poly[(acrylic acid)-*co*-(2-hydroxyethyl acrylate), (COOH)]-*link*(-CO-NH-)-[(1), $(NH_2)_{Lys}$, octreotide]})

Note1: In this example, the composition is unknown but the order of conjugations directly attached to the support is imposed by the synthesis protocol.

Note 2: The support is a copolymer, so the name is constructed from the copolymer and not from poly(acrylic acid). If the same conjugate was made from poly(acrylic acid), an extra conjugation would contribute, but the name would lead to the same graphical representation in the absence of information on composition and distribution of constitutional repeating units.

Case 3:

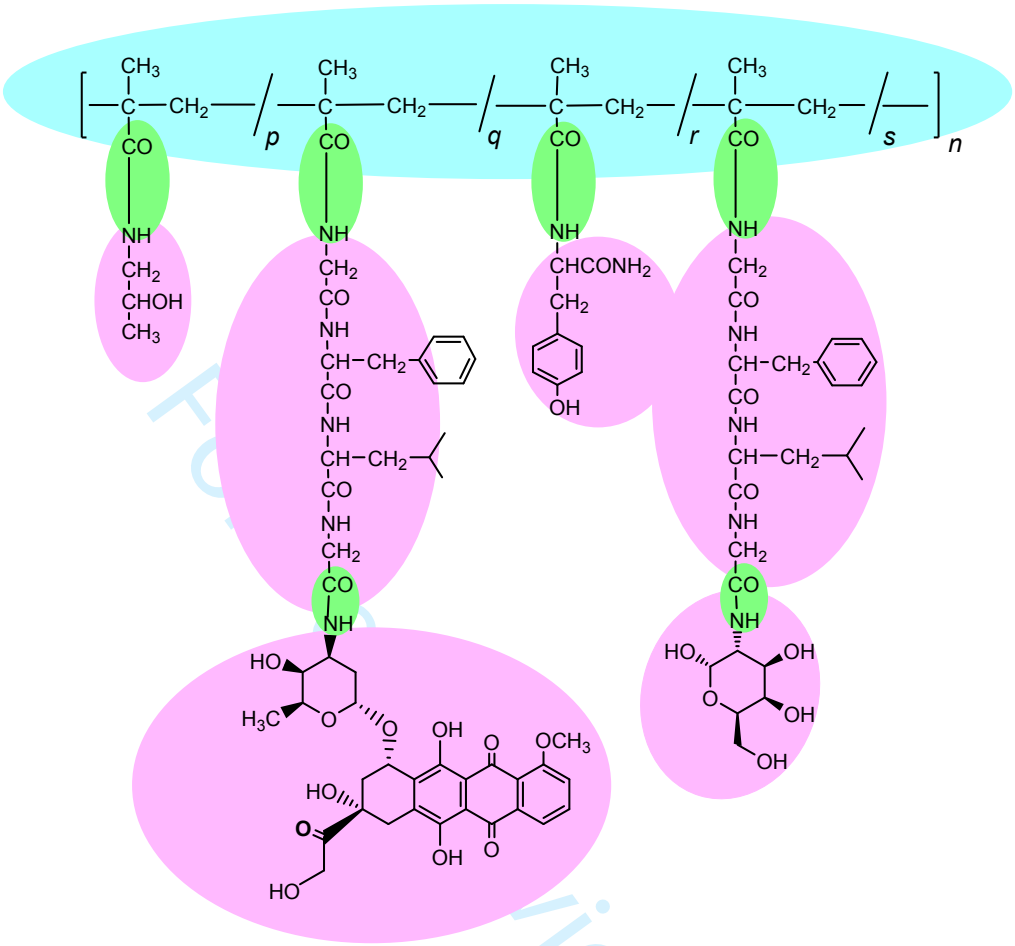

Fig. 9: Complex conjugate in which poly(methacrylic acid) repeating units act in different extents as substrates for different unique or multiple conjugations, each playing a specific role: (*p*) ones provide hydrophilicity and water solubility; (*q*) ones bear a drug that can be released enzymatically by the enzymatic cleavage of the tetrapeptide active spacer arm; (*r*) ones allow labelling by iodine to monitor the fate of the complex *in vivo*; and (*s*) ones bear galactosyl as the ligand to target specific receptors borne by hepatocytes [9].

IUPAC conjugate name:

conj({[poly(methacrylic acid), (COOH)]-*link*(-CO-NH-)-{[(q), (NH_2), Gly-Phe-Leu-Gly, (COOH)]-*link*(-CO-NH-)-[(1), (NH_2), doxorubicin]}, -{[(s), (NH_2), Gly-Phe-Leu-Gly, (COOH)]-*link*(-CO-NH-)-[(1), (NH_2), galactosamine]}, -{[(p), (NH_2), 1-aminopropan-2-ol]}, -{[(r), (NH_2), tyrosine amide]})

Case 4:

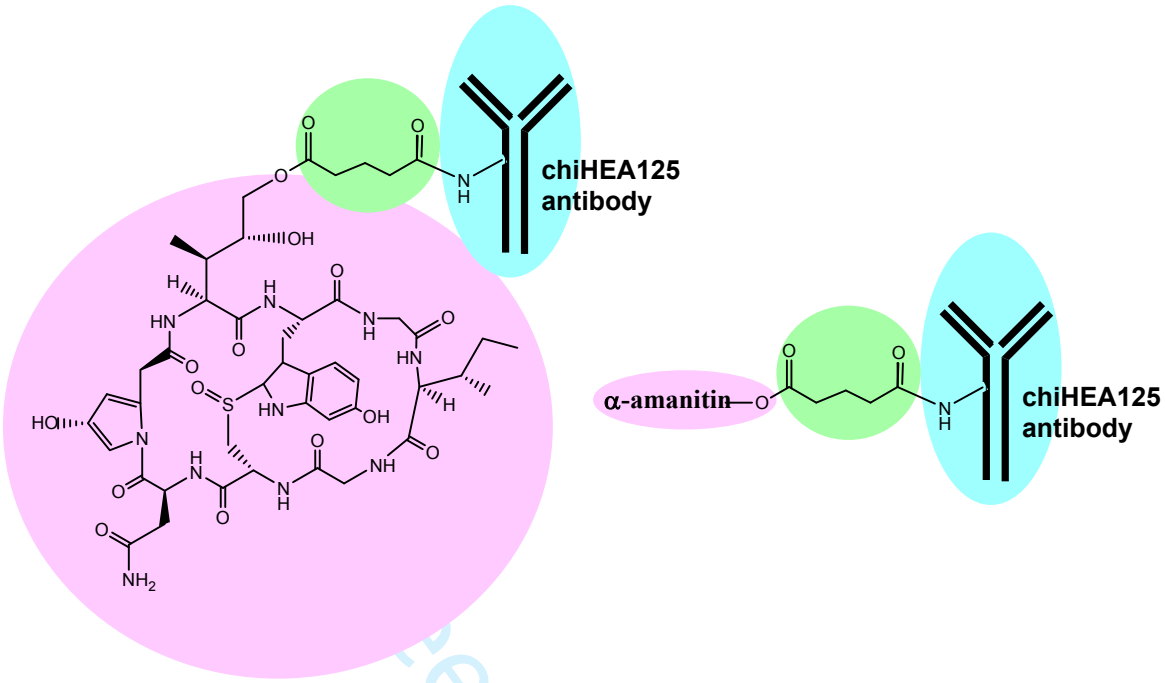

Fig. 10: Conjugate of α-amanitin, an amatoxin from mushroom, connected to the chiHEA125 chimerized antibody using pentanedioic acid as the link. [10].

IUPAC conjugate name:
conj([chiHEA125 antibody, $(NH_2)_{Lys}$]-*link*(-NH-CO-)-{[(COOH), pentanedioic acid, (COOH)]-*link*(-CO-O-)-[(1), (HO-CH_2), α-amanitin]})

Note: In this example, the amine binding site on the antibody is not precisely localized.

Case 5:

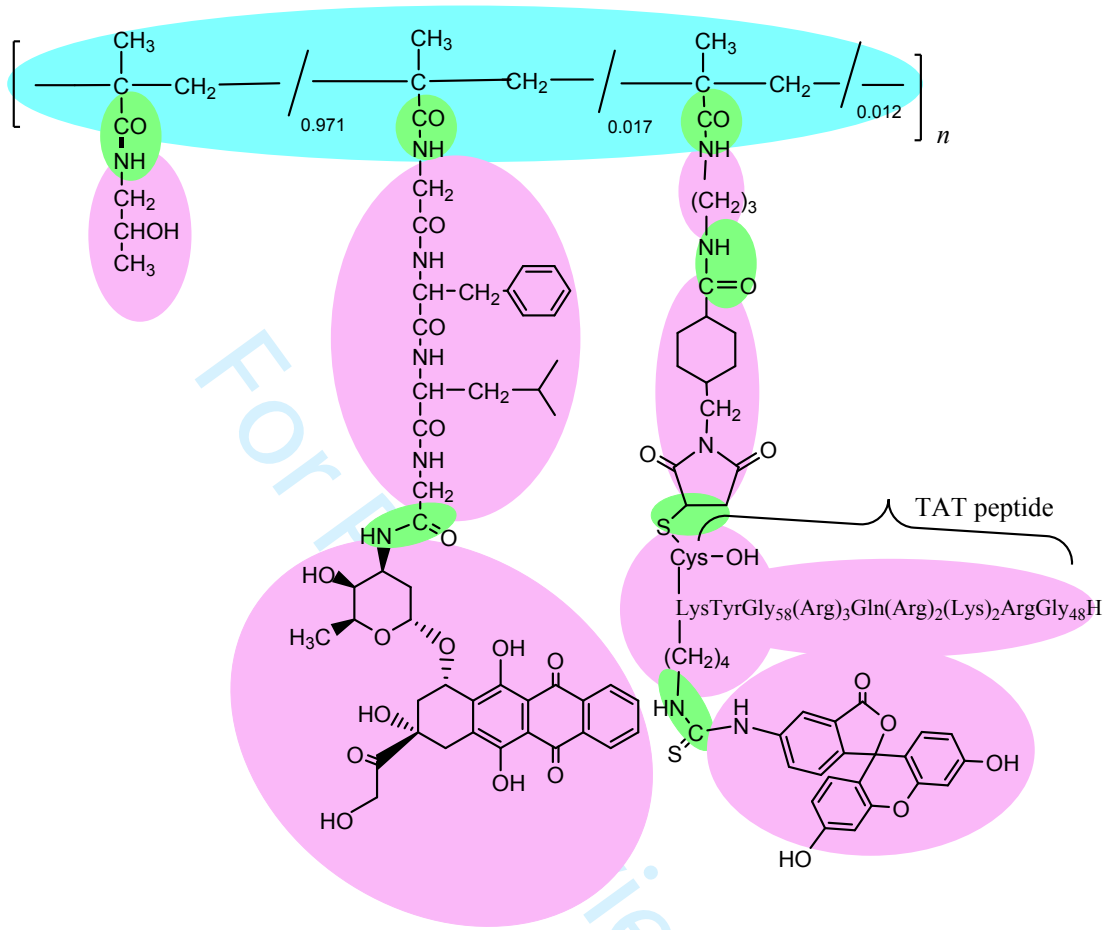

Fig. 11: Complex conjugate based on poly(methacrylic acid) bearing 1-aminopropan-2-ol (solubilizing group), doxorubicin (drug), and a targeting TAT peptide [Cys61-Tyr-Lys-Gly-$(Arg)_3$-Gln-Arg-Arg-Lys-Lys-Arg-Gly58)] labelled using fluorescein isothiocyanate (FITC). The tetrapeptide that links the drug to the carrier is an enzymatically cleavable active spacer arm selected to release doxorubicin. In contrast, the long junction between the labelled TAT peptide and the carrier is only a link composed of 1,3-diaminopropane that provides two amine functional groups, one for binding to the carrier and the other for binding the succinimidyl(4-(*N*-maleimidomethyl)cyclohexane-1-carboxylic acid that provides a C=C double bond to easily react with the SH of the TAT cysteine [11].

IUPAC conjugate name:

conj([poly(methacrylic acid), (COOH)]-*link*-(-CO-NH-)-[(0.971), (NH_2), 1-aminopropan-2-ol], -{[(0.017), (NH_2), Gly-Phe-Leu-Gly, (COOH)]-*link*(-CO-NH-)-[(1), (NH_2), doxorubicin]}, -{[(0.012), (NH_2), 1,3-diaminopropane, (NH_2)]-link(-NH-CO-)-[(1), (COOH), succinimidyl 4-(*N*-maleimidomethyl)cyclohexane-3-carboxy, (C=C)]-*link*-(-CH-S-CH-)-[(1), $(HS)_{Cys61}$, TAT peptide, $(NH_2)_{Lys60}$]-*link*-(-NH-CS-NH-)-[(1), (S=C=N),fluorescein 5-isothiocyanate]})

Membership of sponsoring bodies

Division IV

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Membership of the Subcommittee on Polymer Terminology during the preparation of these Recommendations (2014–2019) was as follows:
Chair: R. C. Hiorns (France), from 2014; **Secretary**: C. K. Luscombe (USA), 2014-2015; P. D. Topham (UK), from 2016; **Members**: V. Abetz (Germany); R. Adhikari (Nepal); G. Allegra (Italy); M. Barón (Argentina); R. Boucher (UK); P. Carbone (UK); M. C. H. Chan (Malaysia); T. Chang (Korea); J. Chen (USA); C. Fellows (Australia); A. Fradet (France); F. Giuntini (UK); C. F. O. Graeff (Brazil); J. He (China); K.-H. Hellwich (Germany); M. Hess (Germany); P. Hodge (UK); W. Hu (China); J.-I. Jin (Korea); R. G. Jones (UK); J. Kahovec (Czech Republic); D. Keddie (UK); T. Kitayama (Japan); P. Kratochvíl (Czech Republic); P. Kubisa (Poland); C. K. Luscombe (USA); M. Malinconico (Italy); P. Mallon (South Africa); J. B. Matson (USA); S. V. Meille (Italy); J. Merna (Czech Republic); G. Moad (Australia); W. Mormann (Germany); T. Nakano (Japan), C. K. Ober (USA); M. Peeters (UK); S. Penczek (Poland); O. Phillipova (Russia); M. D. Purbrick (UK); G. Raos (Italy); G. Russell (New Zealand); C. G. dos Santos (Brazil); C. Scholz (USA); S. Słomkowski (Poland); R. F. T. Stepto‡ (UK); N. Stingelin (UK); A. Sturcova (Czech Republic); P. Théato (Germany); J.-P. Vairon (France); M. Vert (France); J. Vohlídal (Czech Republic); M. G. Walter (USA); E. S. Wilks (USA); M.-H. Yoon (Republic of Korea).

Division VIII

Membership of the IUPAC Division of Chemical Nomenclature and Structure Representation for the period 2018–2019 was as follows:
President: A. T. Hutton (South Africa); **Past President**: K.-H. Hellwich (Germany); **Secretary**: R. S. Laitinen (Finland); **Titular Members**: M. A. Beckett (UK); E. C. Constable (Switzerland); T. Damhus (Denmark); R. T. Macaluso (USA); E. Nordlander (Sweden); A. P. Rauter (Portugal); M. M. Rogers (USA); **Associate Members**: E. Mansfield (USA); J. Nagy (Hungary); M. A. Strausbaugh (USA); K. T. Taylor (USA); C. A. Tovee (UK); J. Vohlídal (Czech Republic); **National Representatives**: F. Aricò (Italy); N. Burford (Canada); A. M. da Costa Ferreira (Brazil); S. Erdem (Turkey); S. Koo (Korea); R. Kruszyński (Poland); L. Meesuk (Thailand); M. A. Petrova (Bulgaria); E. Szabó (Slovakia); A. Yerin (Russia); **Ex Officio:** R. M. Hartshorn (New Zealand); G. P. Moss (UK).

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