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Versatile types of hydroxyl-rich polycationic systems via O-heterocyclic ring-opening reactions: From strategic design to nucleic acid delivery applications



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ABSTRACT

Safe and effective vectors play an important role in nucleic acid delivery processes. Ring-opening reactions are quite often used to produce biomaterials with various functions and properties. Instead of surfaceconjugated hydrophilic polymers such as polyethylene glycol, uniformly-distributed hydroxyl groups within one polycation could improve biocompatibility and benefit nucleic acid delivery performances. Hydroxyl groups with uniform distribution are readily produced by ring-opening of O-heterocyclic units. O-Heterocyclic units include cyclic ester (epoxide), carbonate and lactones. Hydroxyl-rich polycationic systems are prepared predominately with aminated poly(glycidyl methacrylate) (PGMA). PGMA is the most common epoxy polymer and can be post-modified readily via epoxide ring-opening reactions by different amine species. Hydroxyl-rich polycationic systems are also reported by ring-opening polymerization between various epoxy and amine units. In addition, post hydroxylation of polycations via different O-heterocyclic ring-opening reactions could give rise to various hydroxyl-rich polycationic systems. More recently, versatile types of hydroxyl-rich polycationic systems with special molecular and topological structures, such as linear, star-shaped, comb-shaped, supramolecular, branched, hierarchical, and hetero-nanostructured carriers, are well studied. This review summarizes recent research activities in hydroxyl-rich polycationic systems. Their different design strategies via O-heterocyclic ringopening reactions and unique nucleic acid delivery applications are described in detail. The research activities indicate that hydroxyl-rich polycationic systems become versatile and powerful candidates for the development of advanced multifunctional delivery systems of nucleic acids.

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Nomenclature ABO Amino-1-butanol Ad Adamantane **AEPP** N-(Aminoethyl)piperazine AIE Aggregation-induced emission APBA Aminophenylboronic acid APO Amino-2-propanol APP N-(3-Aminopropyl)-2-pyrrolidinone **APTES** 3-Aminopropyl-triethoxysilane **ATRP** Atom transfer radical polymerization Gold A11 BD 1.4-Butanediamine BIBA α -Bromoisobutyric acid BIBB 2-Bromoisobutyryl bromide BIP-OH 2,6-Bis(1-methylbenzimidazolyl)-4hydroxypyridine BMA N-Butylmethylamine BSA Bovine serum albumin CA Cystamine CD Cyclodextrin CD/5-FC Cytosine deaminase/5-fluorocytosine **CEST** Chemical exchange saturation transfer CHO Cholesterol ε-Caprolactone CL CNC Cellulose nanocrystal **CPT** 10-Hydroxyl camptothecin CTComputed tomography 1D One-dimensional DEA Diethylamine DED N,N-Dimethylethylenediamine DET Diethylenetriamine Dipropylamine DPA **DTPA** Diethylenetriaminepentacetate acid EΑ Ethanolamine ED 1.2-Ethanediamine **EHDO** 5-Ethyl-5-(hydroxymethyl)-1,3-dioxan-2-oxo EP Epichlorohydrin **ESCC** Esophageal squamous cell carcinoma FA Folic acid FM Functional molecules **GSH** Glutathione II Iohexol intermediate LA α-Lipoic acid **LCPA** Linear cyclen-based polyamine **MEA** Methylethylamine

```
MRI
        Magnetic resonance imaging
        N-Methylpropylamine
MPA
NIR
        Near-infrared
NR
        Nanorod
QD
        Quantum dot
PA
        Propylamine
PAMAM Polyamidoamine
PAI
        Photoacoustic imaging
PBA
        Phenylboronic acid
PBI-OH
        N,N-Bis(2-[2-hydroxyethoxy]ethyl)perylene-
         3,4,9,10-tetra carboxylic acid bisimide
Pc
        Phthalocyanine
PDM
        Poly((2-dimethyl amino)ethyl methacrylate)
pDNA
        Plasmid DNA
PDT
        Photodynamic therapy
PEH
        Pentaethylenehexamine
PEG
        Polyethylene glycol
PEI
        Polyethylenimine
PER
        Pentaerythritol
PGEA
        EA-functionalized PGMA
PGED
        ED-functionalized PGMA
PGMA
        Poly(glycidyl methacrylate)
ы
        Phosphatidylinositol
POEAA
        Poly(ortho ester amino alcohol)
PP
        Piperazine
PPEGEEMA Poly(poly(ethylene glycol)ethyl ether methacry-
        late)
PTT
        Photothermal therapy
RE
        Rare-earth
SAR
        Structure-activity relationship
SHNP
        Starlike hollow silica nanoparticle
siRNA
        Short interfering RNA
t-Boc
        t-Butoxycarbonyl
TACN
        1,4,7-Triazacyclononane
TAE
        Tri(β-aminoethyl)amine)
TAPc-Zn Zinc(II) tetraaminophthalocyanine
TEP
        Tetraethylenepentamine
TET
        Triethylenetetramine
TGIC
        1,3,5-Triglycidyl isocyanurate
TMC
        Trimethylene carbonate
TMED
        N,N,N'-Trimethylethylenediamine
TPE-OH Hydroxyl-containing tetraphenylethene
TRE
        Tris(2-aminoethyl)amine
UCL
        Up-conversion luminescence
VE
        Vinethene
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