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Review

# A toolbox of building blocks, linkers and crystallisation methods used to generate single-chain magnets

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ABSTRACT

Single-molecule magnets (SMMs) and single-chain magnets (SCMs) are potential candidates for more dense data storage and quantum computing as well as providing interesting systems with which to study the physics behind molecular magnetism. Despite only being discovered in 2001, the field of SCM is experiencing rapid growth and already shows promise with regard to improving on the blocking temperatures ($T_B$) achievable by SMMs. Indeed, to date, the record $T_B$ values for SCMs vs SMMs are running neck and neck, at 14 K vs 13.9 K, respectively. This review details the range of building blocks and linkers that, prior to 1 January 2014, have been used to prepare complexes that were reported to be SCMs. Then, as X-ray structure determinations are of crucial importance, a summary of the crystallisation methods

*Abbreviations:* 1D, one dimensional; 2D, two dimensional; 3D, three dimensional; MOF, metal organic framework; SCM, single-chain magnet; SMM, single-molecule magnet; $T_B$, blocking temperature.

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Ising centres
1D-chains
Crystal structures
Crystallisation methods

that can be used to assemble the building blocks (usually Ising centres) and linkers into 1D chains, in the form of single crystals, is provided. A table summarising the building blocks/linkers and crystallisation methods, CSD codes, and key magnetic parameters, for the SCMs reported pre-2014, is provided as a useful resource for researchers in this field. The reader is referred to previous excellent reviews for a description of the theory and terms used in the field of SCM: this review instead takes a synthetic chemists perspective, presenting the components and crystallisation methods employed to generate complexes reported to be SCMs, pre-2014.



**Ligand abbreviations**

Hacac acetylacetone
$H_2$HO-bdc 5-hydroxy-1,3-benzenedicarboxylic acid
Hbdt 5,5′-(1,4-phenylene)bis(1*H*-tetrazol)
bime 1,2-bis(imidazole-1′-yl)ethane
bispicen *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine
$H_2$bispybzt 4-bis(4-carboxypyridinium-1-methyl)benzene
bt 2,2′-bithiazoline
bpa 1,2-bis(pyridin-4-yl)ethane
Hbpca bis(pyridylcarbonyl)amine
$H_2$bpdc benzophenone-2,4′-dicarboxylic acid
bpe 1,2-bis(4-pyridyl)ethylene
bpmh *N*,*N*′-bis-pyridin-4-ylmethylene hydrazine
$H_2$5-Brsalpn *N*,*N*′-propylenebis(5-bromosalicylideneimine)
$H_2$btca benzotriazole-5-carboxylic acid
bpy 2,2′-bipyridine
bpym 2,2′-bipyrimidine
$H_2$Brppz 3-(2-hydroxy-5-bromophenyl)pyrazole
(*M*)-binaba (*M*)-1,1′-binaphthalene-2,2′-bisoxamate
chp 6-chloro-2-pyridinolate
Clppz 3-(2-hydroxy-5-chlorophenyl)pyrazole
$H_2Cl_4$Cat tetrachlorocatechol
5-Cl$H_2$saltmen *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(5-chlorosalicylideneimine)
$H_2$cmpc 1-carboxymethylpyridinium-4-carboxylic acid
1,3-$H_2$cpy 1-carboxymethylpyridinium-3-carboxylic acid
DBF dibutylformamide
DEA diethylacetamide
DEF diethylformamide
$H_2$dhq 2,3-dihydroxyquinoxaline
DMB dimethylbutyramide
dmbpy 4,4′-dimethyl-2,2′-bipyridine
DMF *N*,*N*′-dimethylformamide
DMP dimethylpropionamide
$H_2$dpkd bis(2-pyridyl)methandiol
$H_2$dpkme 1,1-bis(2-pyridyl)-3-methoxy-1,3-propanediol
Hdpam dipyridylamine
Heiao 1-ethylimidazole-2-aldoxime
hetpur 6-amino-9-beta-carboxyethylpurine
Hhfac hexafluoroacetylacetone
HNN 4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide
iPr-Pybox 2,2′-(2,6-pyridinediyl)bis(4-isopropyl-2-oxazoline)
$H_2$Mepybzt 1-carboxymethylpyridinium-4-benzoic acid
5-Me$H_2$saltmen *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(5-methylsalycylideneimine)
$H_2$Meppz 3-(2-hydroxy-5-methylphenyl)pyrazole
Hmiao 1-methylimidazole-2-aldoxime
Mp 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene
6-MeHpy 6-methylpyridine-2-carbaldehydeoxime
$H_2$napthcx *N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldehydene)-*trans*-diaminocyclohexane
$H_2$napthem *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(naphthylideneimine)
$H_2$napthpn *N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldehydene)-1,3-diaminopropane
NITPhOMe 4′-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide
NITPhOBu 4′-butoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide
NITThienPh (5-phenyl-2-thienyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide
3-OMe$H_2$salpn *N*,*N*′-propylenebis(5-methoxysalicylideneimine)
3-OMe$H_2$salen *N*,*N*′-ethylenebis(3-methoxysalicylideneimine)
5-OMe$H_2$salen *N*,*N*′-ethylenebis(5-methoxysalicylideneimine)
4-OMe$H_2$salox 2-hydroxy-4-methoxysalicylaldoxime
HOAc acetic acid
$H_2$ox oxalic acid
TCNQ tetracyanoquinodimethane
TCNE tetracyanoethylene
4,4-Hopybz 4-(4-pyridyl)benzoic acid *N*-oxide
(*R*)-$H_2$pabn (*R*)-*N*(2),*N*(2′)-bis(pyridin-2-ylmethyl)-1,′-binaphthyl-2,2′-diamine
Hpao pyridine-2-aldoxime
Hpcq 8-(pyridine-2-carboxamido)quinolone
2,5-$H_2$pidc pyridine-2,5-dicarboxylic acid
Hpiv pivalic acid
Hpyoa 2-(pyridin-3-yloxy)-acetic acid
Ph phenyl group
py pyridine
pzTp tetrakis(pyrazolyl)borate
Hsalox 2-hydroxysalicylaldoxime
3-tBu-5-Me$H_2$salox 2-hydroxy-3-*tert*-butyl-5-methoxysalicylaldoxime
tBu-$H_2$salox 3,5-di-*tert*-butylsalicylaldoxime
$H_2$saltmen *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(salycylideneimine)
5-TMAM$H_2$salen *N*,*N*′-ethylenebis(5-trimethylammoniomethyl)bis(salicylideneimine)
$H_2$TPP *meso*-tetraphenylporphyrin
$H_2$TBPP *meso*-tetra(4-biphenyl)porphyrin
$H_2$TFPP tetrakis(*ortho*-fluorophenyl)porphyrin