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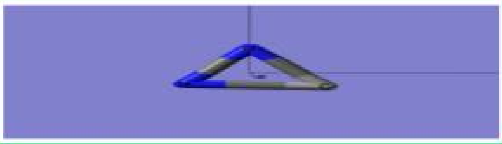
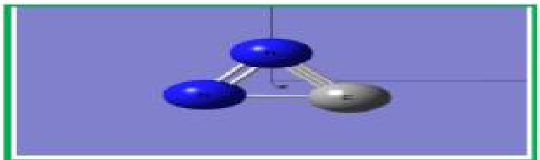
New Chemistry News

$^{-}N=C=N^{-}$



New News of Chem (NNC)



ChemNewsNew (CNN)

CNN–39

Dynamic covalent bonds (chemistry)

Information Source	ACS.org ; sciencedirect.com
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I. Object oriented terminology (OOT) for Dyn.Cov.Bond

II. Select Research Titles(2000 to2021) in Dyn.Cov.Bond

KLab

rsr.chem1979

Dynamic Covalent Bonds

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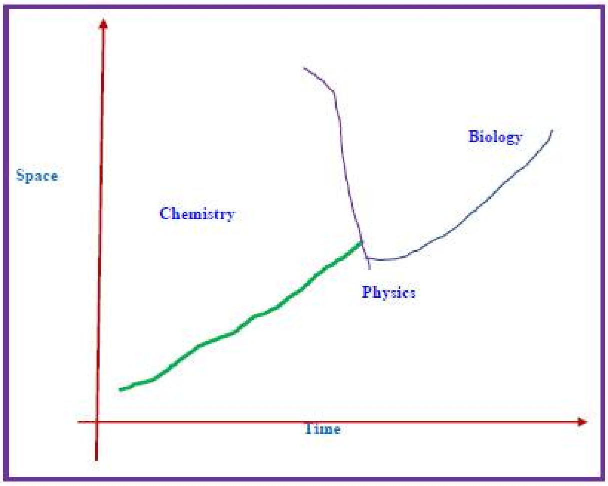
Chemical bonds	
Covalent bonds	☞ Static ☞ Dynamic
Dynamic bonds	☞ Supramolecular or Non-covalent interactions ☞ Dynamic covalent bonds

Dynamic covalent bonds
o Dynamic covalent bonds
o Orthogonal covalent bonds
o 2,3,4,more
o Dynamic covalent Reaction
o Dynamic Covalent (bond) Chemistry
o Orthogonal dynamic covalent chemistry
o Dynamic Covalent Chemistry + Systems Chemistry



Dynamic Covalent Bond	Dyn Cov Bond	DCB

- ✓ These are covalent bonds that are capable of exchanging or switching between several molecules
- ✓ Dynamic bonds reversibly break and reform. They occur autonomously or in response to stimuli
- ✓ Use of dynamic nature of these bonds -- organic synthesis, material science,biomedical applications
- ✓ DCBs in polymeric materials
  - ➔ powerful properties emerge [viz. self-healing, shape-memory increased toughness, ability to relax stresses, change from one macromolecular architecture to another]
- \- certain grey area exists in the definition of the dynamic covalent bonds.

Dyn Cov Bonds

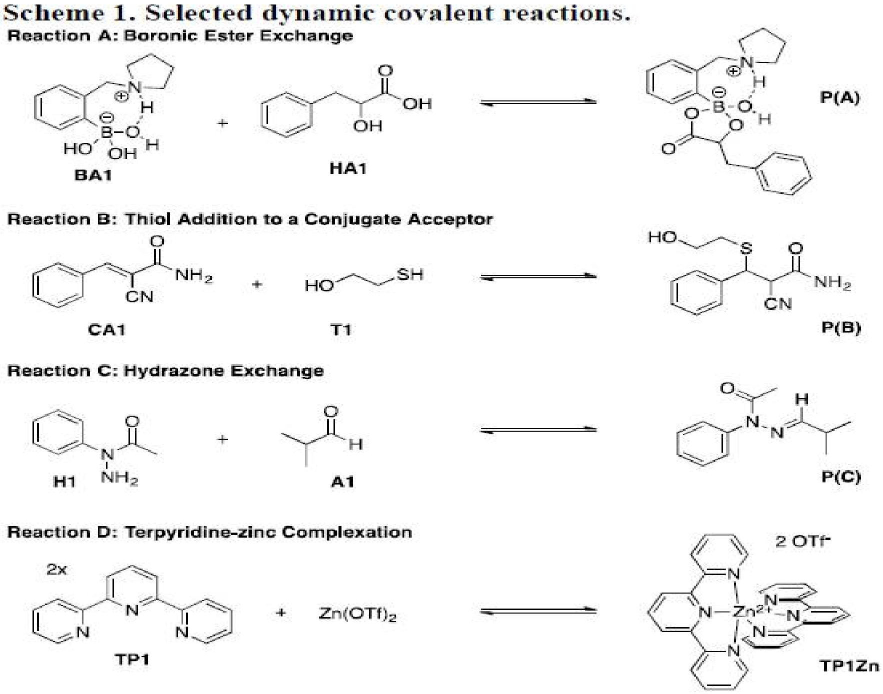
☞Thermodynamic equilibrium -- reversible, tunable, controllable

☞Equilibrium perturbed byphysical/chemical stimuli (temperature, irradiation, and pH)

	Systems: 1, 2, 3, 4	**Quaternary**
	1) Boronic ester exchange **2)** Thiol addition to conjugate acceptor CA1 **3)** Hydrazone exchange **4)** Zinc complexation of terpyridines ☞Medium : methanol and water ☞pH : neutral	☞Reversible under identical reaction conditions ☞Orthogonal i.e. Do not exhibit any cross-reactivity ☞Reactions proceed independently of each other
Appl	➔ Possible to use all four reactions in one pot in a simultaneous, yet orthogonal fashion	

Four dynamic covalent reactions

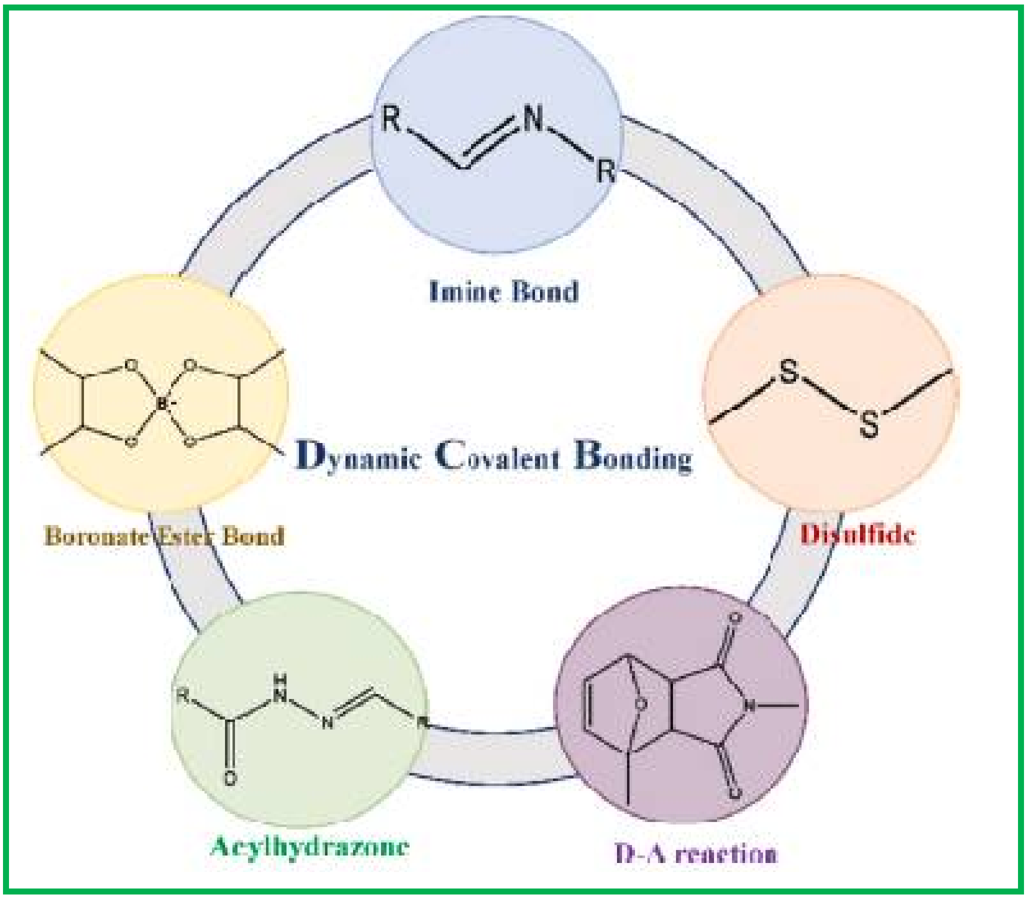
Scheme 1. Selected dynamic covalent reactions.



Binary		**Ternary**		
1	**2**	**1**	**2**	**3**
Boronic ester	Imine	Imine	Boronic ester	Disulfide
Boronic ester	Hydrazone			
Disulfide	Imine			
Disulfide	Hydrazone			

Dyn Cov Bonded atoms and groups

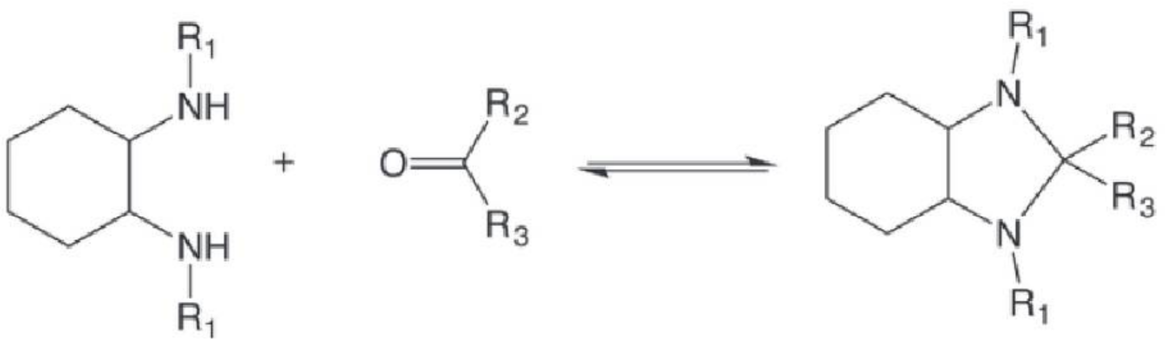
N,O,	S,Se	C	
Imine	Disulphide	Cabon-to-carbon	C-C C = C
Hydrazone	Selenide		
Acylhydrazone			
Amides			
Oximes			



Imine bond: formed by the condensation of aldehydes or ketones with ammonia or primary amines or vicinyl secondary amine.

- ✓ These are considered as formation reactions.
- ✓ Schiff reported first the compound (later popular as Schiff's base) with imine bond.
- ✓ Many biocompatible materials like chitosan, gelatin collagen with imine bonds find biomedical applications

Schiff base formation between aldehyde and amine



Aminal formation between a ketone and two secondaryamines

- Unstable chemical bond
- Imine bond also interact with other DCBs

Hydrazonebonds: Hydrazone bonds are formed by polycondensation of aldehydes or ketones with hydrazine. The linkages in hydrazone structures are comparatively more complex than the imines

- ✓ These are one of the classical C-N dynamic covalent bonds extensively in use of fabrication of drug delivery systems.
- ✓ Hydrazones provide the acid-activatable property in drug conjugates.

Ex: A multicomponent system with three different DynCovBonds viz

- ✓ hydrazone, disulfide and borate, used in for optoelectronic signal generation/detection, interface, device manufacturing

Ex: Two dynamic cross-linking methods ofacylhydrazone bond and Pluronic micellar cross-linking are made into a hydrogel system

- + Excellent mechanical properties and self-healing ability
- + Application: tissue engineering

Acylhydrazonebonds: formed from acylhydrazine and aldehydes or ketones in acidic medium or at high temperature in presence of a catalyst.

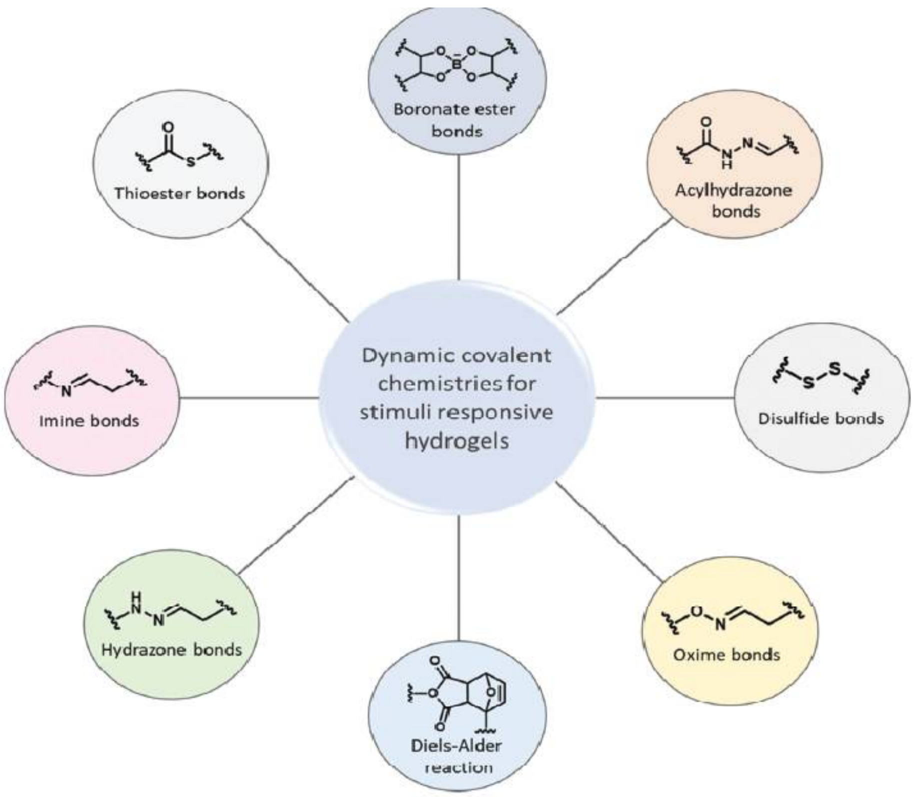
- ✓ Appl: preparation of DynCov BondedHydrogels
- ✓ Acylhydrazone-based drugs
  - o Nitrofurazone, nitrofurantoin, carbazochrome,
  - o Nifuroxazide, dantrolene, and azumolene

Amides: The amide linkers (cis-aconitamide, citraconamide, and maleamide containg maleic acid derivatives) are acid-responsive

- Appl: Drug Delivery Systems
- **Ex:** polycaprolactone-modified cisplatin prodrug-conjugated poly(amidoamine) dendrimers
- →clustered Nano Particles formed
- Platinum prodrug-dendrimers released in the acidic microenvironment of tumor
- It penetrates deep into the tumor tissue efficiently
- With the enhanced uptake of tumor cells, the cisplatin restored from the prodrug by glutathione (GSH) reduction to perform antineoplastic activity

Oximes: Formed by condensation of aldehydes orketones with hydroxylamine or O-alkyl substituted compounds.

- Compared with imide / acylhydrazone bond, it has stronger stability and better mechanical properties
- Used to develop acid-responsive Drug Deliv Syst.
- **Ex:** Gene therapy of cancer--- nucleic acids delivered into cells efficiently through the cell surface engineering. oxime bonds are present in nucleic acid/lipid nanocomplexes



Dynamic covalent bonds in hydrogels – These are stimuli responsive

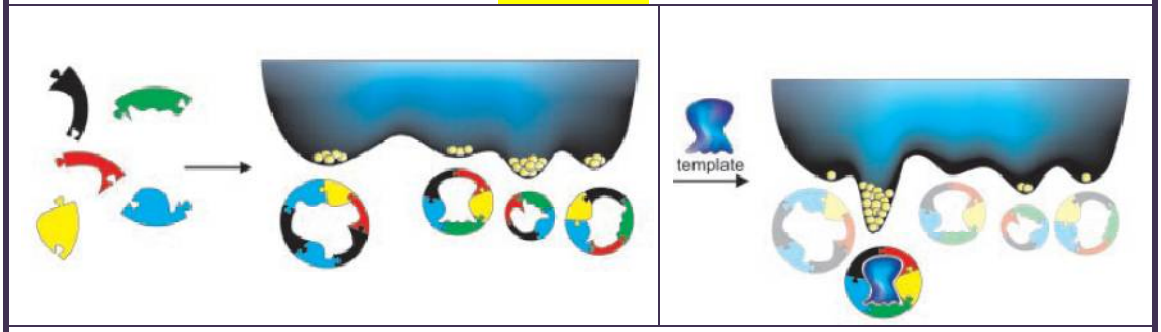
Dynamic covalent Reaction	Dyn Cov React	DCR

- Dynamic covalent reactions usually have slower kinetics
- Require catalysts to attain rapid equilibrium.
+ Scope of dynamic covalent reactions rapidly expanding
- Limitations: Reversible reactions suitable for DCvC are still very limited

Dynamic covalent Library	**Dyn Cov Libr**	DCL
New research discipline	o Equilibration processes o With kinetically controlled chemical or physical steps ▪ Including catalysis and autocatalysis + o Dynamic covalent Libraries	

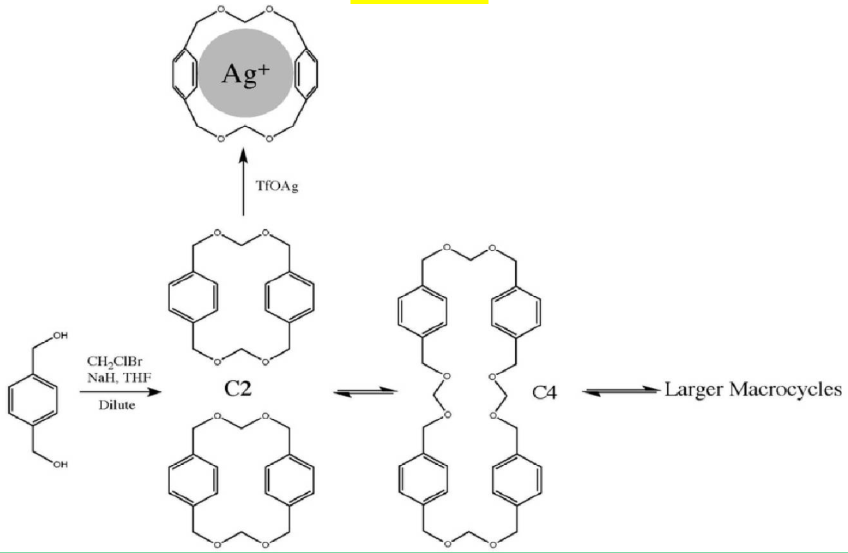
	Thermodynamic template effect in (macrocycle) synthesis
Thermodynamic template	A thermodynamic templateis a reagent that stabilizes one product over all others. **Expl:** It is a consequence of lowering it's Gibb's free energy(ΔG°) template complex in relation to other products

Illustration 1



Effect of adding a template that strongly and selectively binds to one of the equilibrating species on free energy landscape

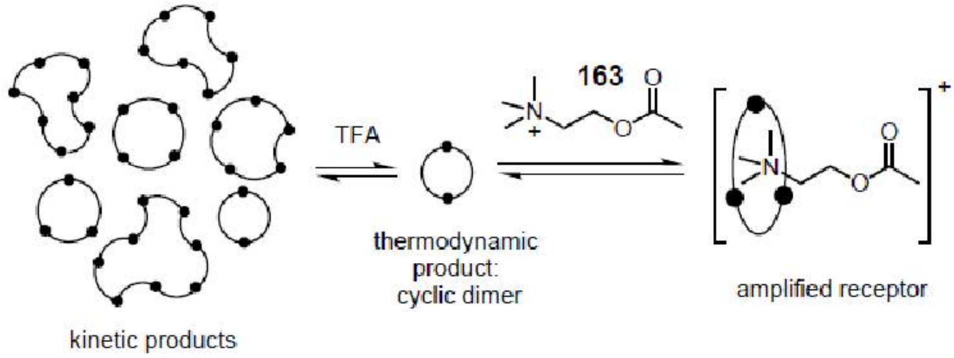
Illustration 2:

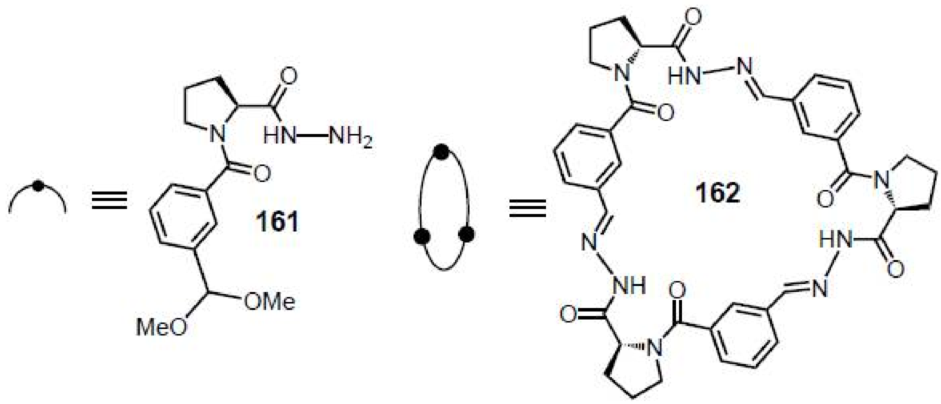


Step 1: Reaction of a diol + chlorobromomethane + sodium hydride→ cyclophane C2
Step2:Acidcatalyzed (triflic acid) transacetalization of C2 → C4

If	Transacetalisation catalyst is silver triflate
Then	silver ion fits ideally and irreversiblyin the C2 cavity

Thermodynamic and/or kinetic controlled products





- Cyclization of 161
- Subsequent proof-reading and templating of the DCL→ thermodynamically favored cyclic dimer (major product)
- Introduction of 163 templates →formation cyclic trimer.

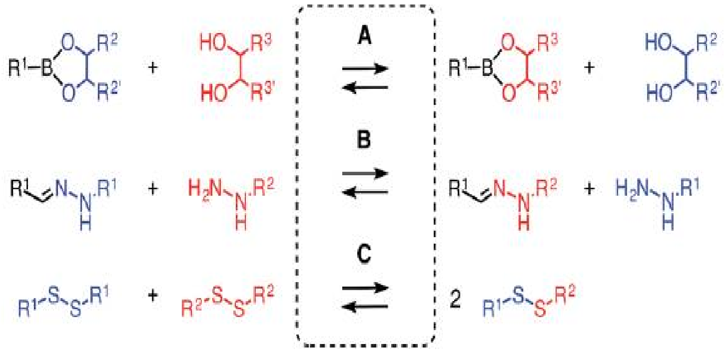
Dynamic Covalent Chemistry		Dyn Cov Chem	DCC
Dynamic Covalent (bond)→Chemistry			
Dynamism	in Dyn Cov Chem	is within molecules through ☞ Reversible formation and ☞ Breaking of covalent bonds under thermodynamic control	
	In Supramolecular chemistry	is chemistry is dynamic in the domain beyond molecules through ☞intermolecular non-covalent interactions	
Dyn Cov Chem			
Deals with	☞ reversible formation and breaking/scission of covalent bonds ☞ not strong ones within molecules		

Based on	☞ dynamic features of reversible covalent bonds
Combines features	☞ Dyn Cov Chem the error-correction capability of supramolecularchemistry and the robustness of covalent bonding using bottom-up assembly.
Appl	☞ synthetic chemists' strategy to prepare complex supramolecular assemblies from discrete on homo-sequenced type molecular building blocks - Majority of DCvC reactions rely of chemistry i.e. hetero-sequenced reactions relatively less explored
Appl	☞ Material science ☞ Molecular separation ☞ Chemical biology ☞ Medicine ☞ Drug discovery ☞ Biotechnology
Proof-of-concept	Delivered + Sparkling exiting output + Unexpected outcome + Happened time and again
Limitations	- Early definitions of DCC considered only systems atequilibrium - Functional properties exhibited by equilibrium systems are dwarfed by those of far-from equilibriumsystems.

Orthogonal protective groups in org synthesis		**Ortho Protect Group**	**OPG**
Orthogonal protecting group strategy	iff	▪ both protective groups are present in the same molecule & ▪ it enables selective deprotection of one protected amino group for a reaction & ▪ second protected amino group remains untouched	

Orthogonal multilevel dynamic libraries		
Ortho Multilevel Dyn Lib#	iff	Reversible processes operateindependently 📖Ex. imine formation + metal ion coordination 📖 Ex. imine formation + intramolecular rearrangement
Non- otho Multilevel Dyn Lib	iff	Processes may interfere or cross over 📖Ex:, imine formation and Michael addition
✓ # libraries are referred to as orthogonal since two processes do not interfere ✓ Analogy: orthogonal protecting groups in organic chemistry		

Orthogonal Chemical Reactions	Ortho Chem React	OCR

Def	✓ Orthogonal chemical reactions are those which do not interfere with each other ✓ Also, do not exhibit cross-reactivity ➔ Employed in reversible covalent and supramolecular chemistry
Orthogonality of conditions	imply that exchange of one without disturbing the others occur Ex. Pair of orthogonal dynamic bonds, hydrazonesand disulfides exchange exclusively under acidic and basic conditions
	Ex: Three orthogonal Dyn Cov Bond reactions  Orthogonality of boronic/boronate esters, hydrazones and disulfides, Selective exchange under conditions A, B, and C ➔ Enables construction and operation of number of doubly dynamic functional systems
Orthogonality in protecting group chemistry	Here, each orthogonal group can be removed inany order depending on the conditions without altering theothers.

Orthogonal dynamic covalent chemistry	Ortho.Dyn.Cov.Chem	ODCC

	☞ It is an offshoot from shadows of dynamic covalent chemistry ☞ In Ortho.Dyn.Cov.Chem, two or more DCvC reactions are combined like in a one-pot synthesis. The high yield complex structured molecular systems are the end products. - Ortho.Dyn.Cov.Chem is less utilized in comparison with Dyn Cov Chem. - Methodology of ODCC is in its infancy Ex. functional group tolerance, general reaction condition ➔ Recent Progress: several challenges have been surmounted
Future	☞ New generation of researchers like anticipated in systems' chemistry ☞ Tools : Multidisciplinary ; Unorthodox ! Predicting exactly where the research will trend and settle ! ---To wait and witness ---- Not even intelligent guess
Possibilistic outcomes	! Discovery of new phenomena or solutions for today's riddles ! Reinterpretation of existing systems

	! Bridging different as yet poorly connected fields ! Development work-flow-line of field ! Most exciting features of Dyn Cov Chem ✓ Proven time and again, is its ability to deliver ➔ Unexpected exiting, sparkling output

Dynamic Covalent Chemistry + Systems Chemistry	**Dyn Cov Chem + Syst Chem**	**DCC + SC**
	(Super) Hybrid approach ➔ Hyper connection nets between chemistry, biology, nanotechnology + Nature mimic development of research work-method-flow + Complexity, emergence of unforeseen outcome + Complement to a traditional (but advanced matured to human limits)practices in chemistry where ! [emphasis being on single, high yield, pure compounds]	

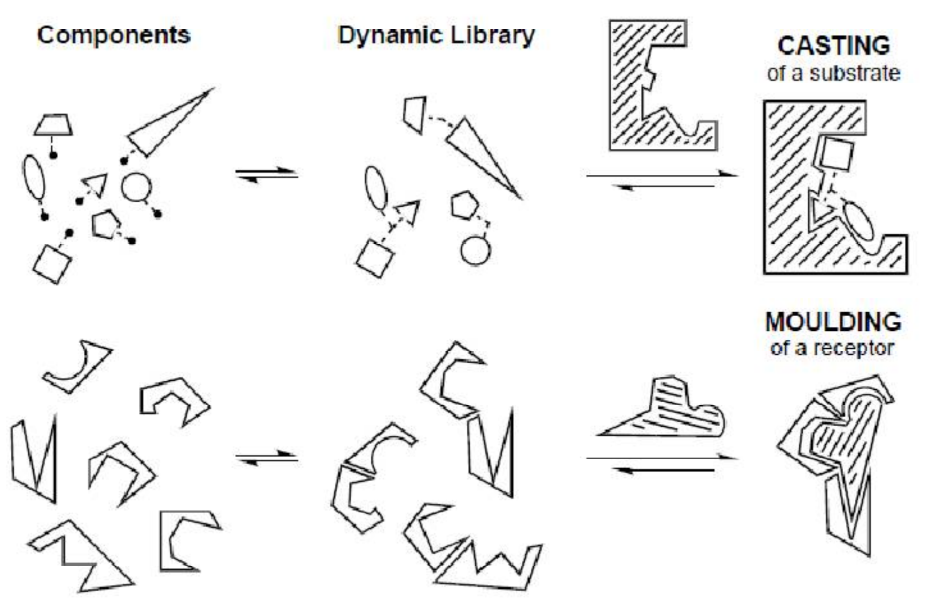
$$$Library
➔ Chemical compound Library
➔ Spectral library
➔ Property & Response Library

$$$Library
➔ Virtual compound Library
➔ Dynamic compound Library
➔ Constitutional Dynamic library
➔ Combinatorial library

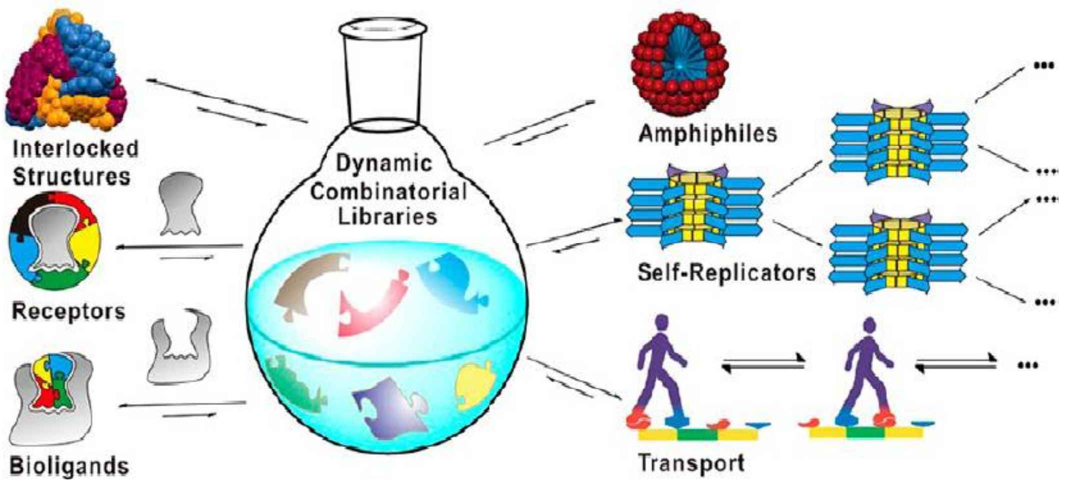
Dynamic Combinatorial $$$
➔ Dynamic Combinatorial Library
➔ Dynamic Combinatorial Chemistry
➔ Constitutional Combinatorial Library

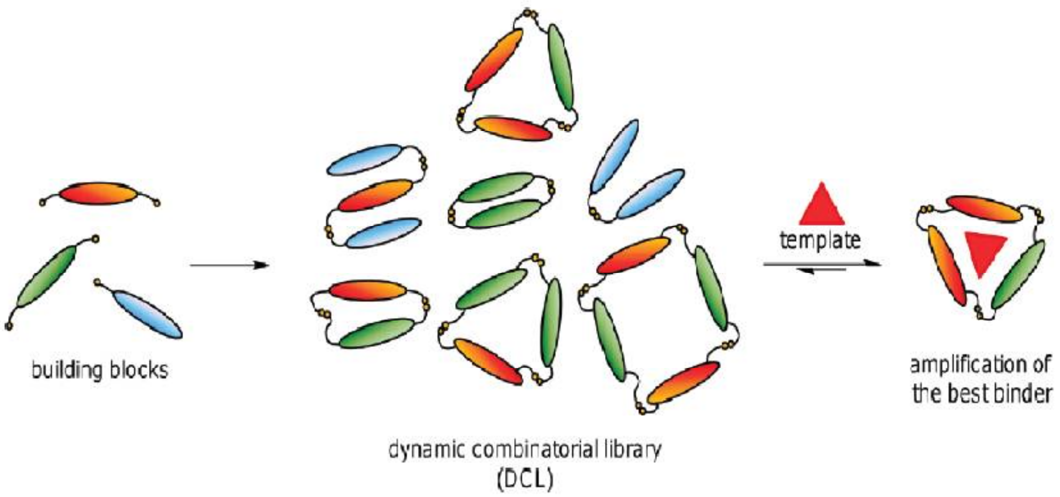
Multilevel Dynamic Libraries
➔ Orthogonal
➔ Non-orthogonal

Dynamic Combinatorial Library		Dyn Comb Lib	DCombLib
Def	☞A library of reversibly interconverting building blocks generated through DynCovChem		
	☞Collection of reversible assemblies of a series of building blocks which undergo o Thermodynamic exchange with each other		
	Library members interconvert by equilibrium processes		
Mechanism	✓ rapid equilibration allows the coexistence of a variety of different species ✓ addition of a proper template will shift the equilibrium toward thecomponent that forms the complex of higher stability (thermodynamic template effect). ✓ when equilibrium is established, reaction conditions are altered to stop equilibration. ✓ optimal binder for the template is then extracted from the reactional mixture by normal laboratory procedures. The property of self-assembly and error-correcting that allow DCvC to be useful in supramolecular chemistry rely on the dynamic property		
Influence of experimental conditions	alter stability of the library members →alter composition of the library.		
Application	DynCombChem ☞ enabled combinatorial pools of candidates to be establishedthrough reversible connections, either by usingcovalent or noncovalent chemistry.		
Caution	! Dynamic combinatorial chemistry and dynamic covalent chemistry are not synonymous		
	☞ dynamic combinatorial chemistry concerns both dynamic covalent hemistry and dynamic noncovalent (supramolecular) chemistry		

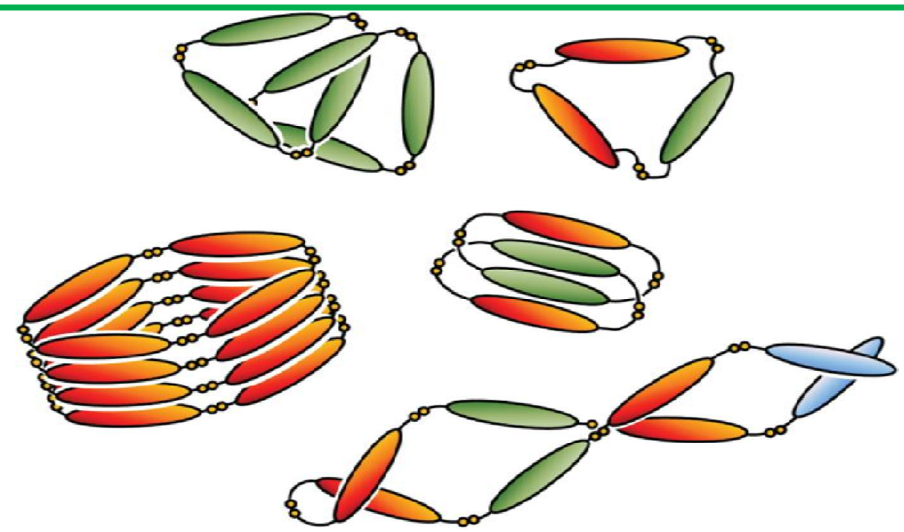


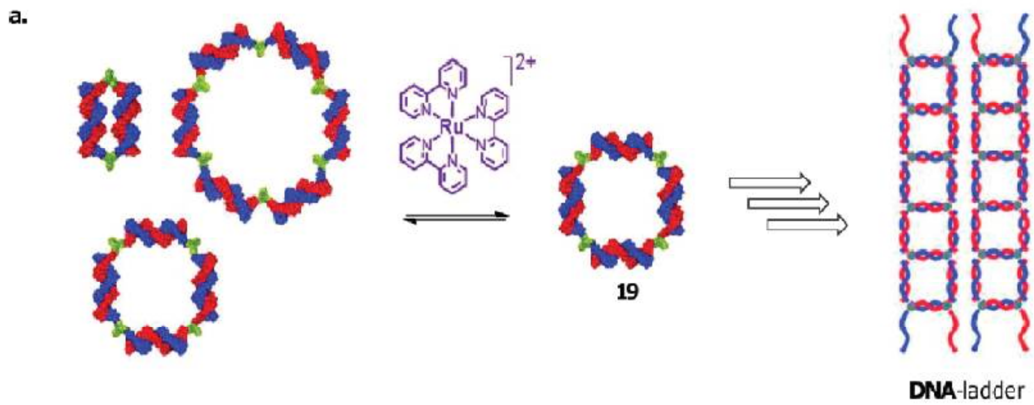
Casting	A macromolecule provides a cavity within which theoptimum ligand may be trapped
Moulding	Ligand collectsthe optimum receptor around itself



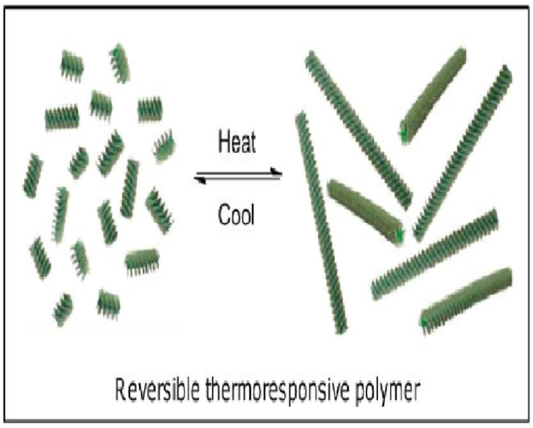


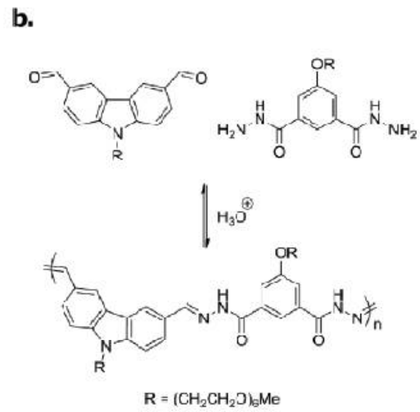
mplification of the best binder in the presence of a template





DNA-based ladder





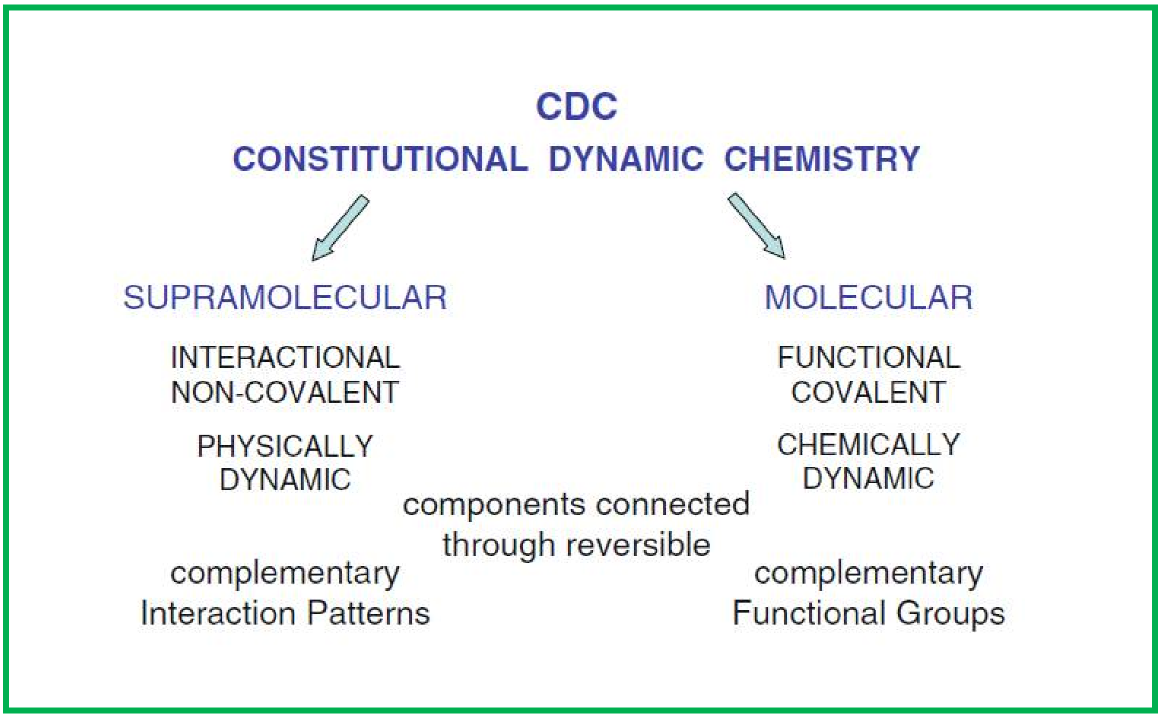
Thermo responsive polymers

Dynamic Combinatorial Chemistry	**Dyn CombChem**	**DCombC**

Def	Dynamic Combinatorial Chemistry deals with chemical systems under rapidly attained thermodynamic equilibrium. It is a is a subset of combinatorial chemistry. o Sanders group and Lehn research school introduced it o It is also called combinatorial supramolecular or molecular chemistry under thermodynamic control
exploits	Reversiblecovalent chemistry to generate combinatorial libraries that are under thermodynamic control
Concerns with	only covalent bonding interactions - As such, it only encompasses a subset of supramolecular chemistries
Implies	library members interconvert continuously by exchanging building blocks with each other

Constitutional Combinatorial Library	**Const Comb Lib**	**ConstCombL**

Molecules	Constitutional dynamic library comprise of a real or virtual set of interconverting supramolecular or molecular entities
Combinome	The full ensemble of all constituents, i.e., of all possible combinations of the components
Genotype	Genotype of the dynamic system comprise of components under consideration
Phenotypes	The sets of constituents generated from these components under given conditions its phenotypes
Modification of composition	Relative amounts of its constituents influenced by parameters: conversion, viz.composition, and expression
Constitutional dynamics	☞ Implies changes in constitution i.e. nature, number, and arrangement of the components of molecular or supramolecular entities ☞ diversity through 🕮 Continuous recomposition, recombination, reorganization, construction, deconstruction 🕮 by either external (incorporation, decorporation, exchange of components) or Internal (rearrangement, reshuffling of components) processes,

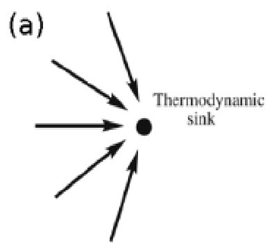


Supplementary information (SupInf)

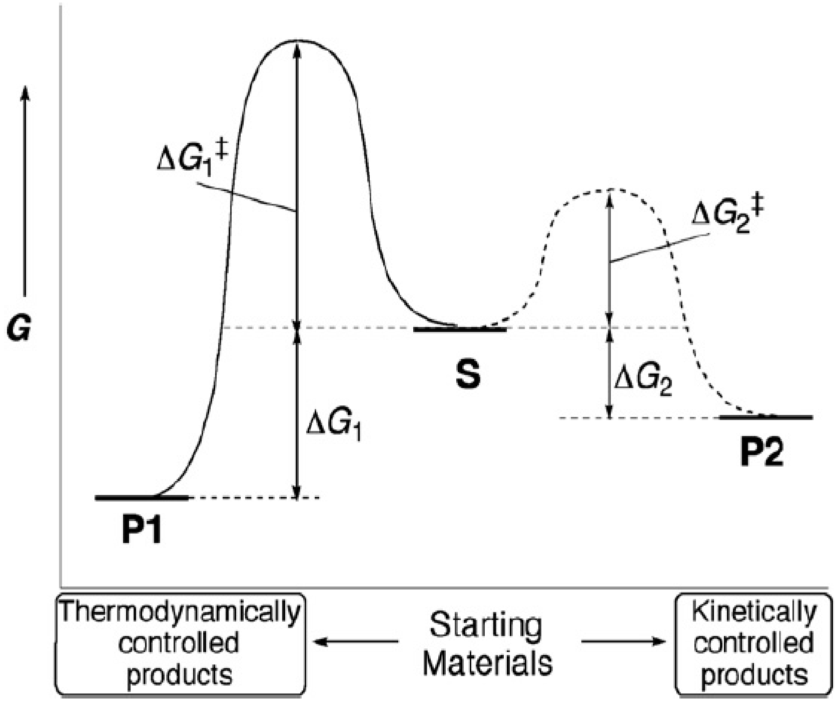
SI-01: thermodynamic and/or kinetic controlled chemical reactions

Stability	Dynamics
Equilibrium	Thermodynamic Control
Irreversible	Kinetic Control
Far from equilibrium	Life processes
✓ Entropy Control	
✓ Thermodynamic and kinetic control	

Regular thermodynamic space

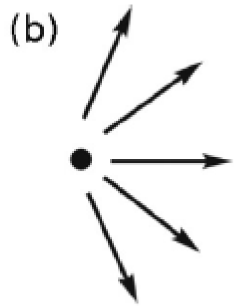


(a) Standard chemical systems are convergent in nature

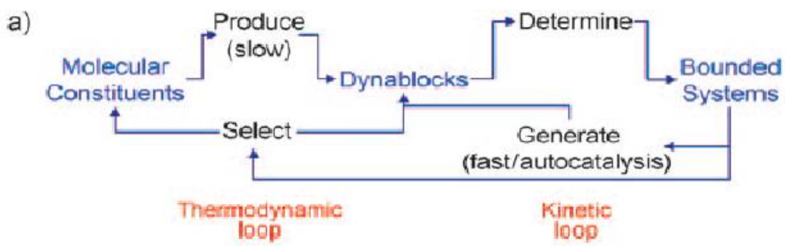


Free energy profils eof competing pathways:
S to P1 (thermodynamic control); S to P2 (kinetic control)

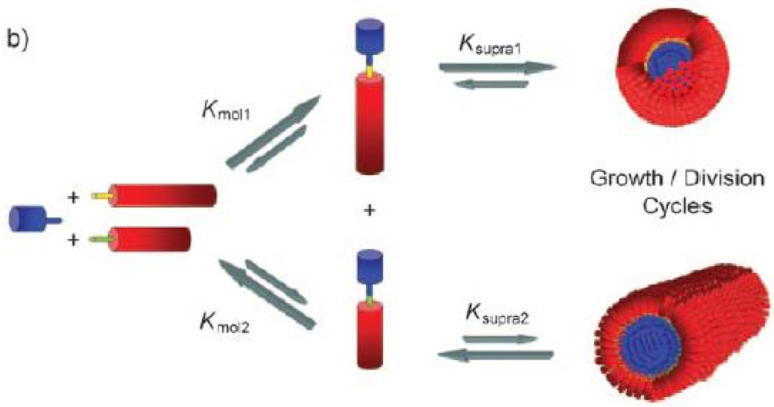
Replicator (Kinetic) space



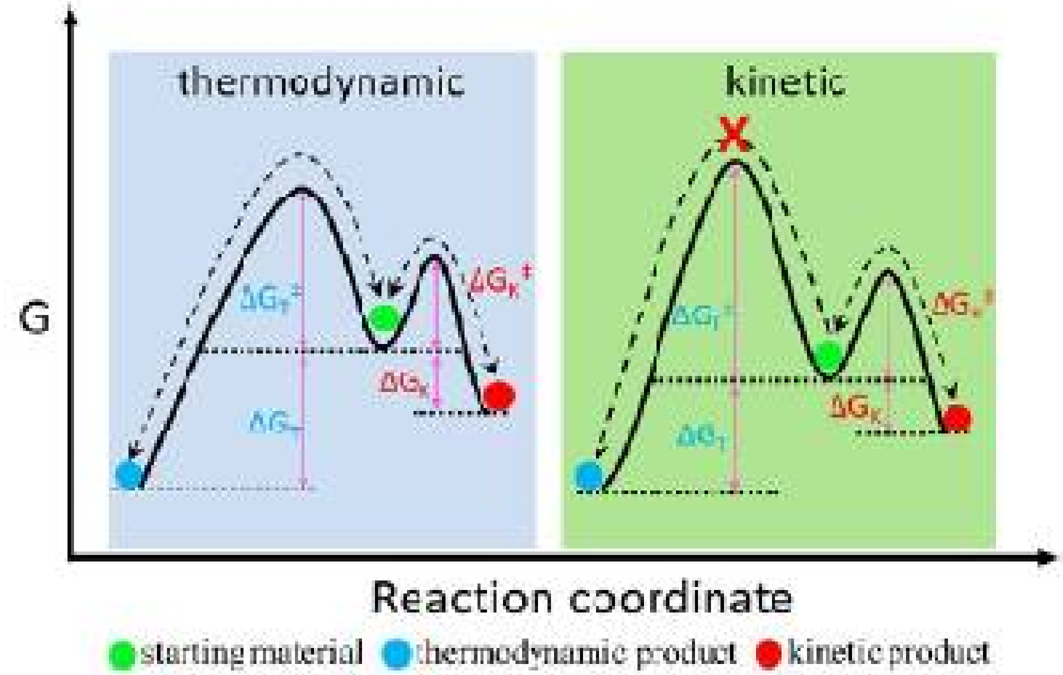
(b) DKS systems are divergent and therefore able to evolve

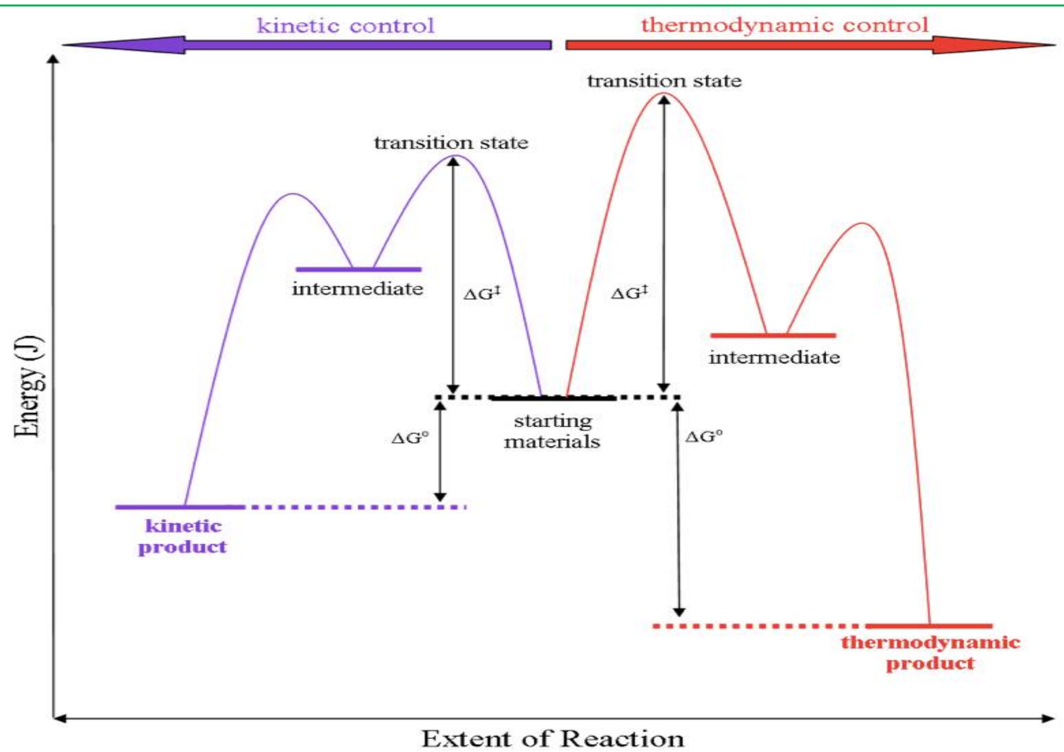


Dynamic combinatorial libraries



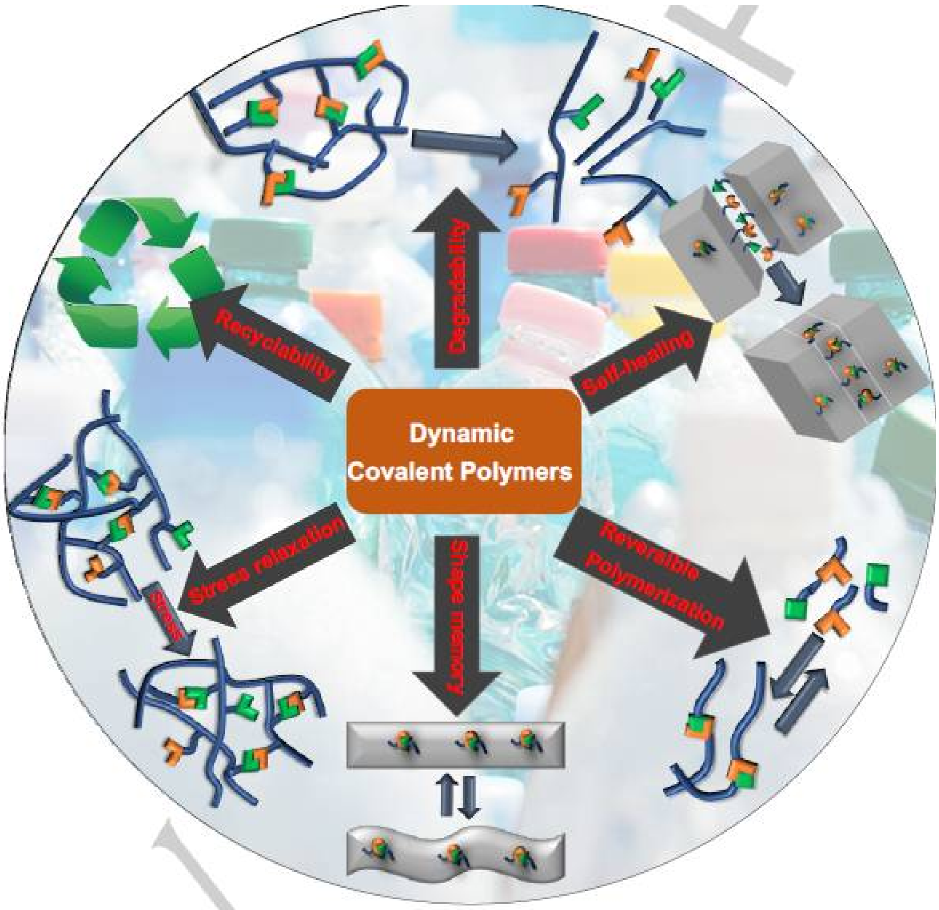
a) Synergistic constitutional relationships observed at two length scales within b) a model minimal self-replicating DCL.





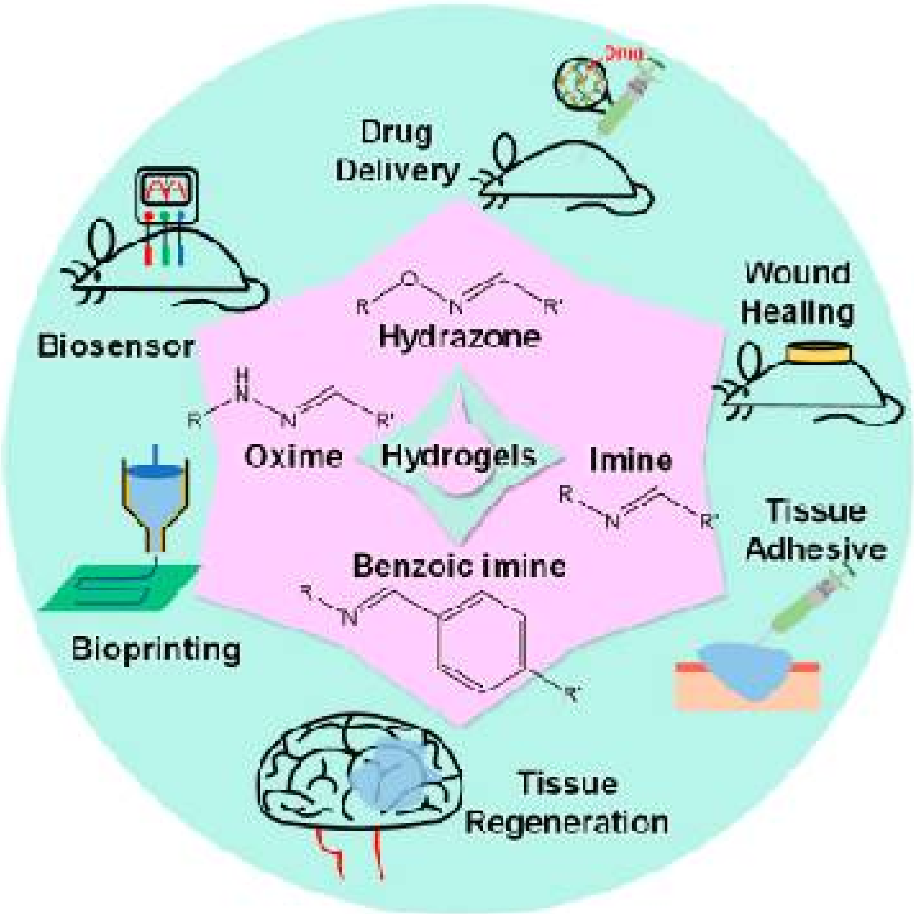
Energy profiles of Reactant → TS → Intermediat →Product
violet (thermodynamic control) ; red: (kinetic control)

SI-02: Polymers -- Dyn Cov Bonds



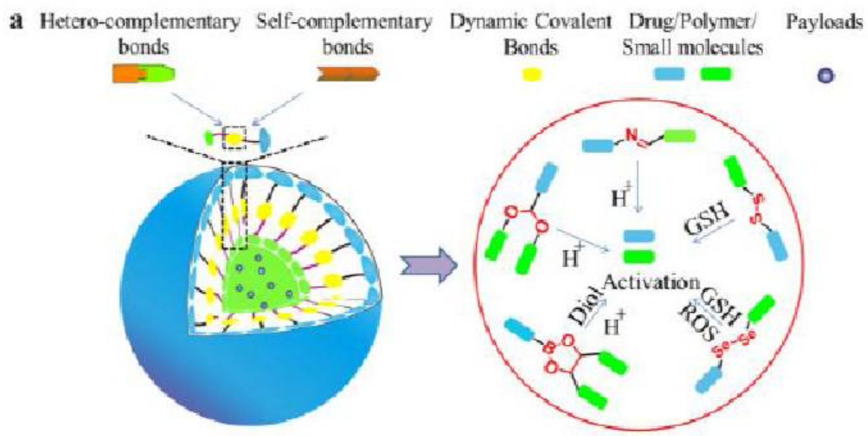
12°: Degradability ; 2°: self-healing; 4°: Reverse polymerisation; 6°: shape memory; 8°: stress relaxation; 10°: recyclability

SI-03:
Biomedical Applications
Hydrogels based on Schiff base linkages

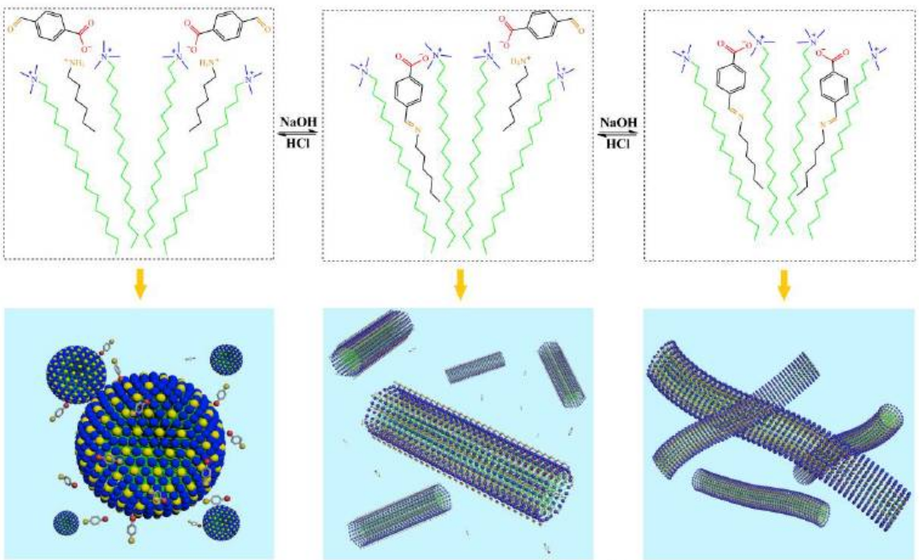


SI-04:
Stimuli-responsive
Drug Delivery systems

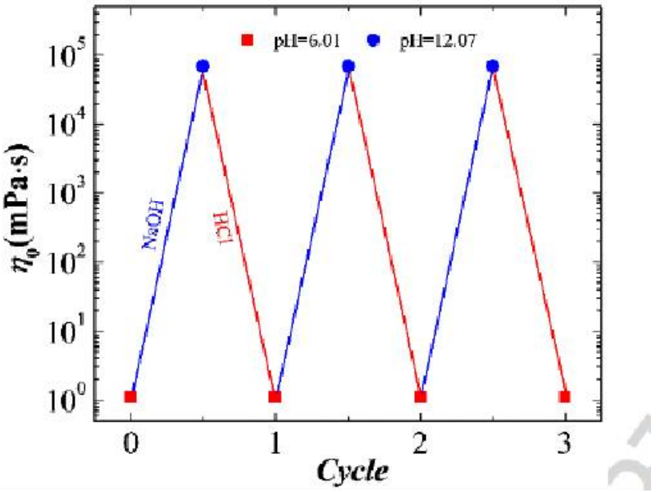
Stimuli	
Based on	
Physics	pH
Chemistry	Concentration
Physical chemistry	Catalyst
Chemical physics	



SI-05:
pH-responsiveCTAB/FA/HA



pH-responsive mechanism of CTAB/FA/HA



pH-reversible viscosity of the CTAB/FA/HA solution

SI-06:
shape-memory performance

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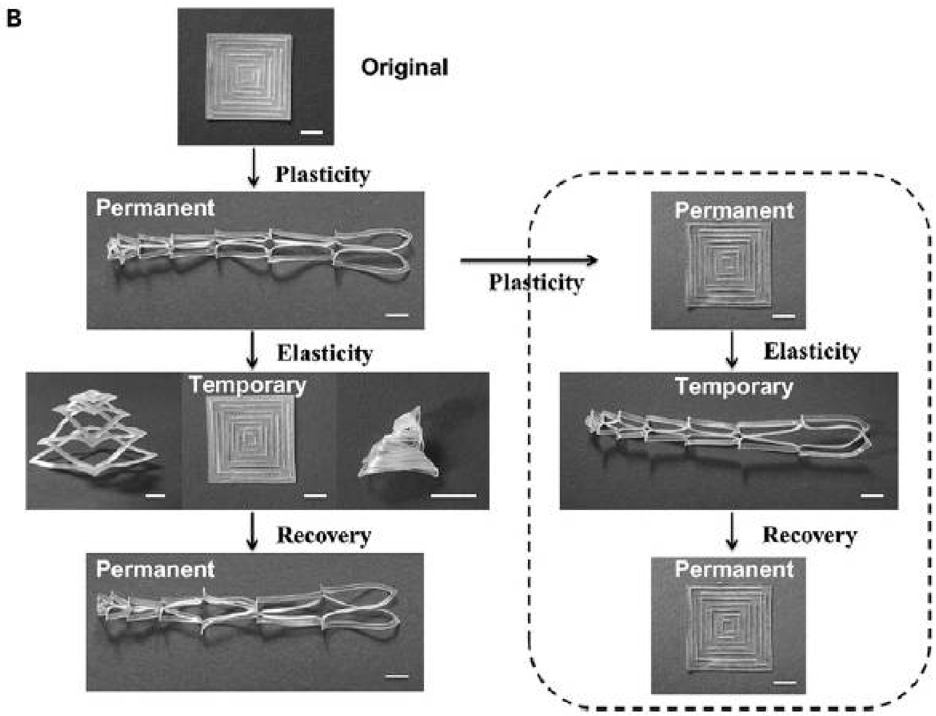
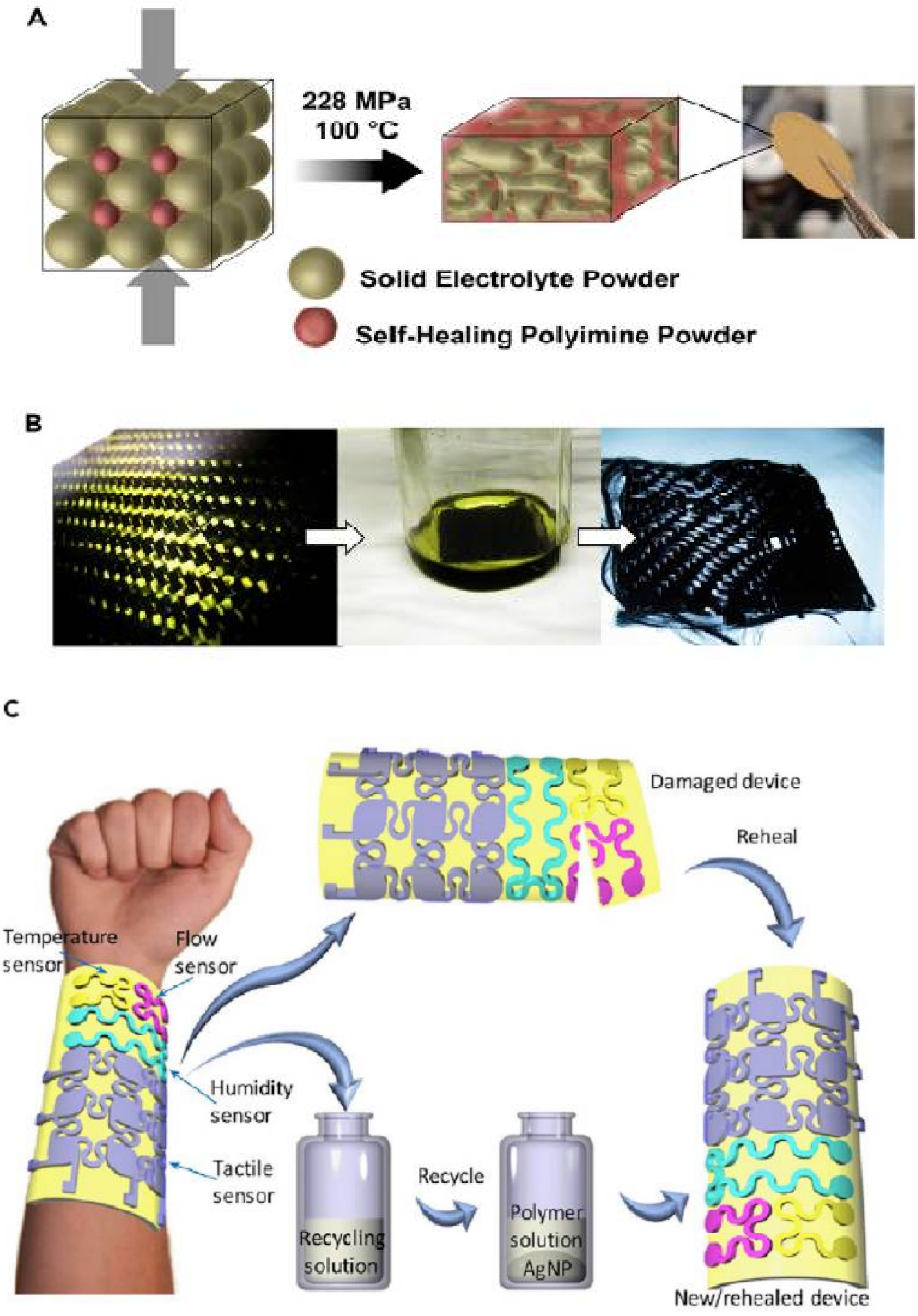


KB: Demonstration of shape-memory performance of P20.	
If	heated above the plasticity temperature (Tv = 130C)
Then	shapes of the polyurethane P20 can be permanently fixed

If	heating above Tg OR below Tv
Then	They deform to various temporary shapes

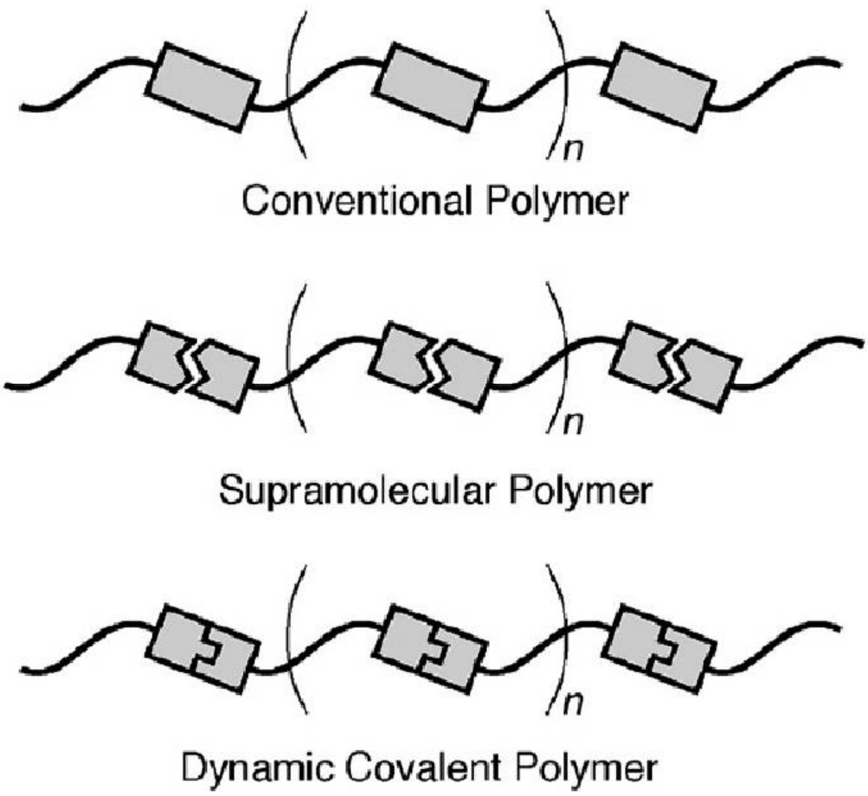
SI-07:
Rehealability and full recyclability of the e-skin

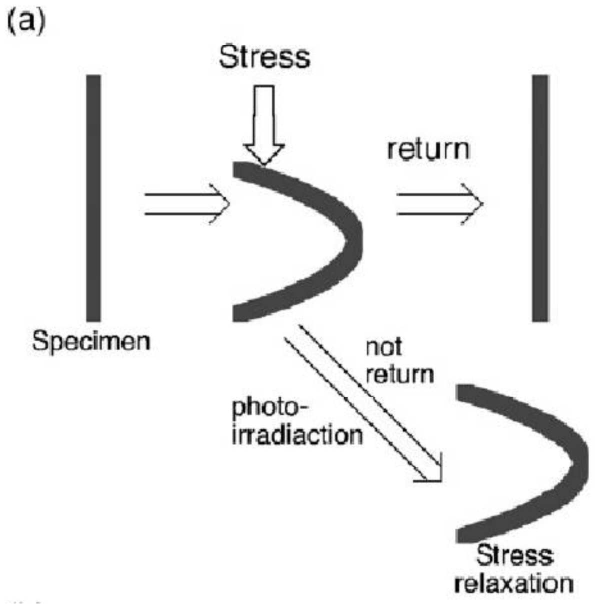


Applications of Malleable Polyimine Thermoset

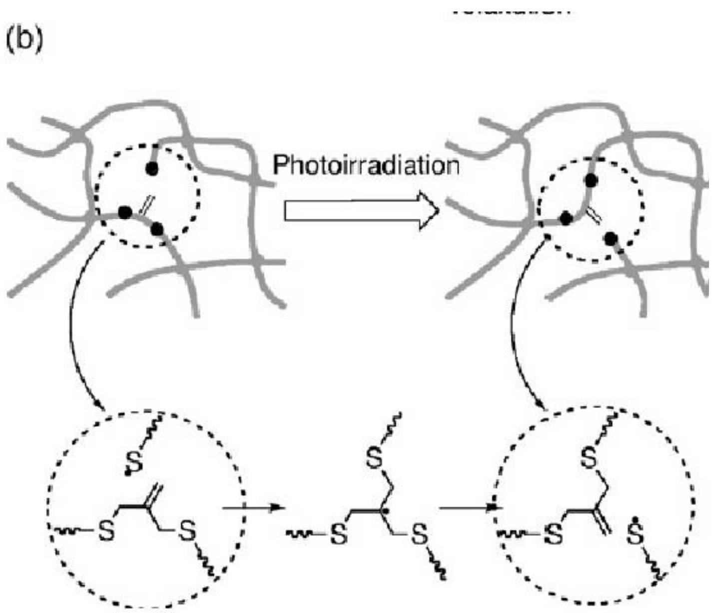
(A) Schematic presentation of the formation of a solid electrolyte-in-polymer matrix membrane
(B) Recycling of full-length carbon fibers from CFRC by simple soaking in neat 34a
(C) Schematic illustration of rehealability and full recyclability of the e-skin

Behavior of a specimen 90



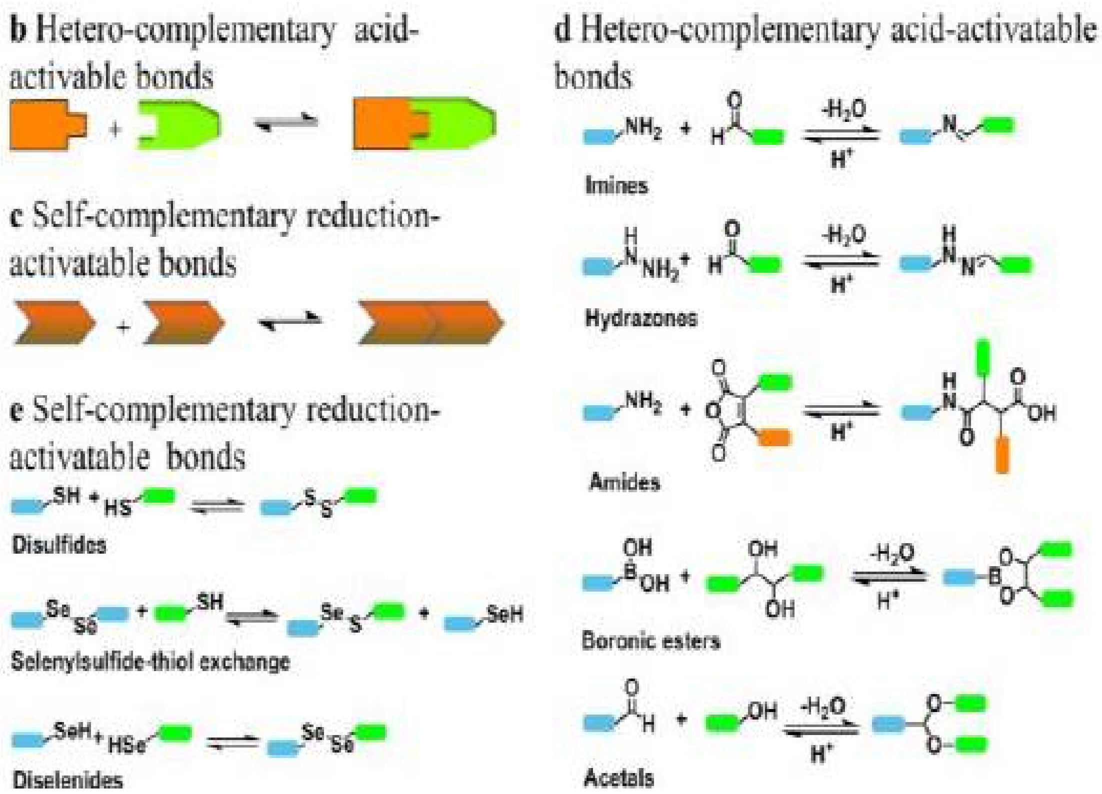


On application of stress with photoirradiation and without photoirradiation



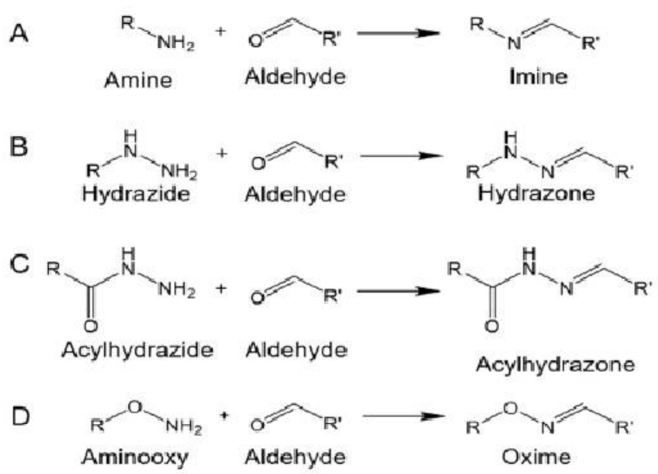
Topological change of the network polymer by chain reaction of allyl sulfide

SI-08:
Dynamic Covalent Complimentary Reactions

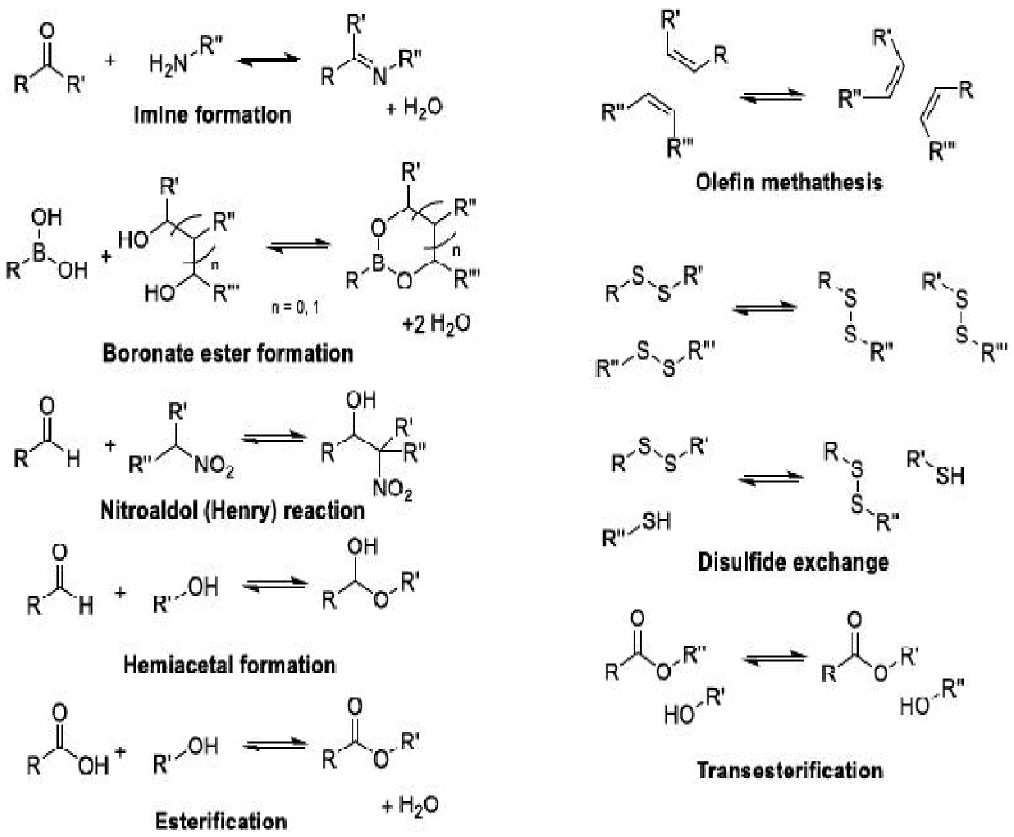


(b) Schematic representation of hetero-complementary acid-activatable bonds;
(c) Schematic representation of self-complementary reduction-responsive bonds;
(d) Representative types of hetero-complementary acid-activatable dynamic covalent bonds;
(e)Representative types of self-complementary reduction-responsive dynamic covalent bonds

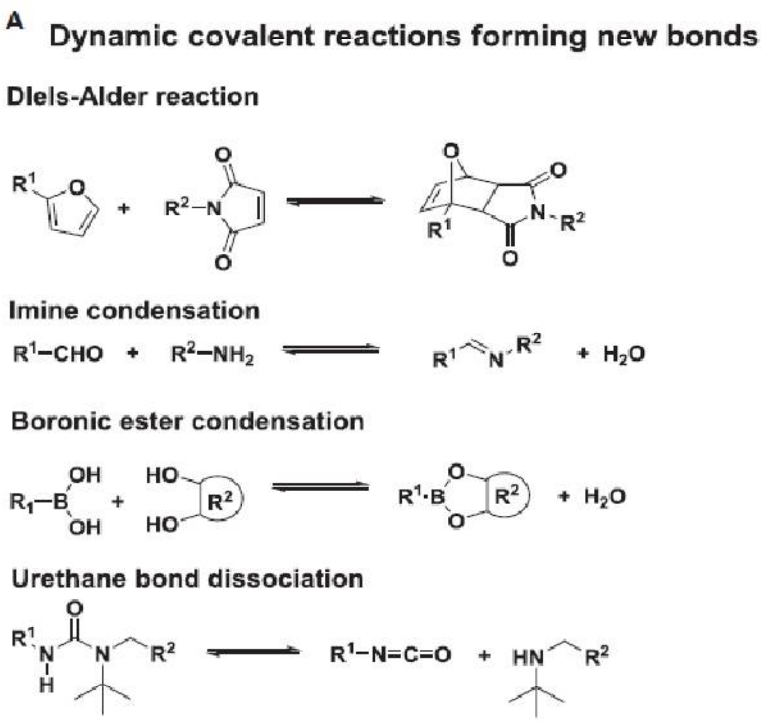
SI-09:
Dynamic Covalent Reactions



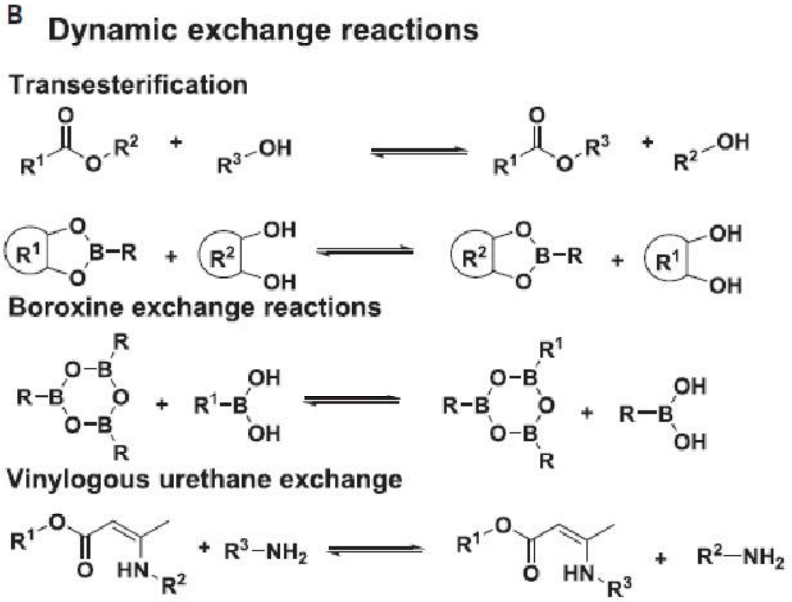
Formation of imine, hydrazone, acylhydrazone, or oxime through reactions between primaryamine, hydrazide, acylhydrazide, or aminooxy and aldehyde



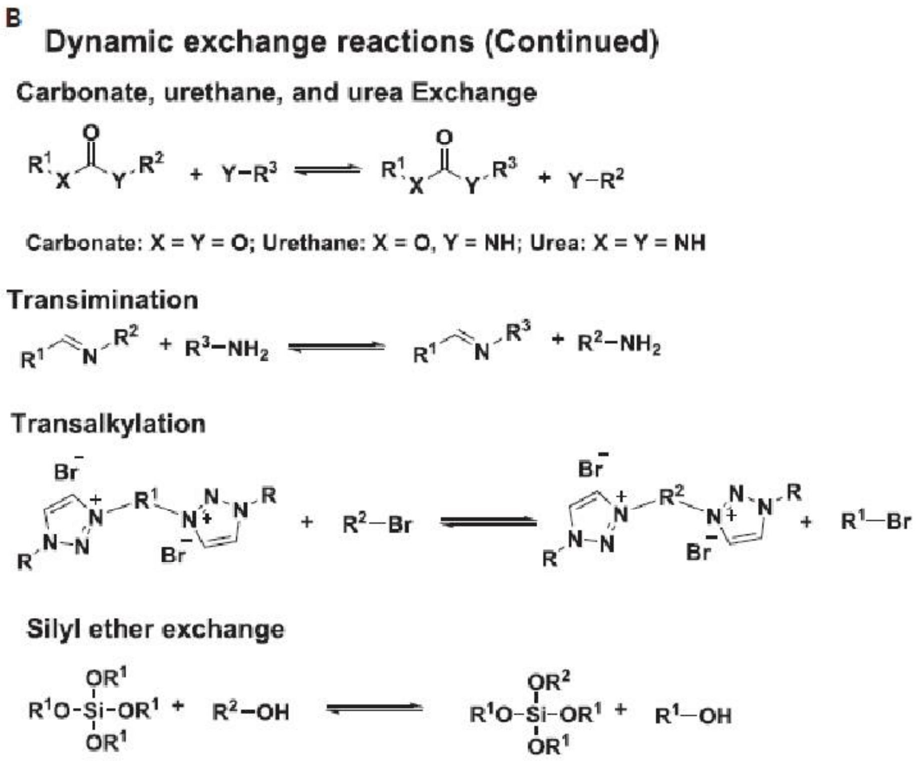
Formation of Borate ester, imine etc.



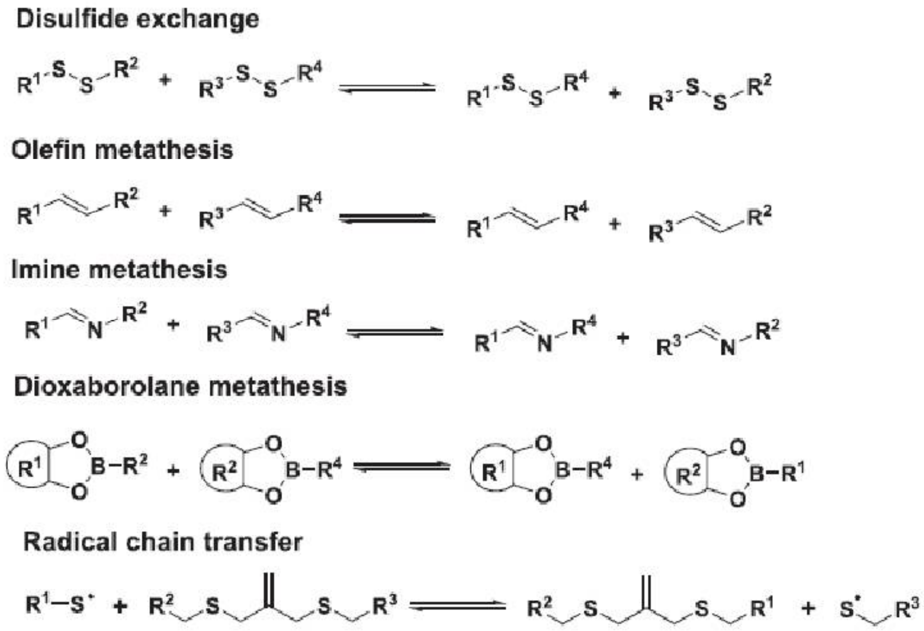
Formation of new bonds



Exchange reactions



Exchange reactions



Exchange reactions

II . Select Research titles (2000 to 2021). …… Dyn.Cov.Bonds ……

Contributions of Nobel Laureatures

Rev		Dyn. Cov.Chem
KeyLrn_Bits	☞ Catenanes ☞ Rotaxanes ☞ Supramolecular chemistry ☞ Polymers	☞ Combinatorial chemistry ☞ Macrocycles

Dynamic Covalent Chemistry	Angew. Chem. Int. Ed. 41(2002), 898-952
Stuart J. Rowan, Stuart J. Cantrill, Graham R. L. Cousins, Jeremy K. M. Sanders and J. Fraser Stoddart	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Biaryl, lactone4		Dyn Cov Bond Dyn Cov Chem, System Chemistry
KeyLrn_Bits	▪ Molecular machines ▪ Molecular motor ▪ Out-of-equilibrium	▪ Chemical energy ▪ Unidirectional rotation ▪ Isomerization ▪ Chirality
Ingenious molecular machines present in living organisms enabling	▪ Motility ▪ Responsiveness	▪ Out-of-equilibrium behaviour
Chemically (biaryl structures) powered rotary molecular motors	▪ Allows complete 360° unidirectional rotation	▪ Based on simple esterification chemistry
Future vision	▪ Design of more sophisticated future artificial machine systems	▪ Driven solely by chemical energy

A Chemically Driven Rotary Molecular Motor Based on Reversible Lactone Formation with Perfect Unidirectionality	Chem, 6(2020)2420-2429 doi.org/10.1016/j.chempr.2020.07.025
Yu Zhang and Zhe Chang and Heng Zhao and Stefano Crespi and Ben L. Feringa and Depeng Zhao	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Reviews

Rev	Functional systems	Orth. Dyn. Cov. Bonds	
to build Functional molecular systems	o Quite unusual o Very demanding o highly original	o Self-sorting o Self-healing o Self-repair o Exchange o Replicate	o Transcribe o Adapt o Adaptive self-sorting o Even walk and ''think'' (logic gates)

Functional systems with orthogonal dynamic covalent bonds	Chem. Soc. Rev., 43(2014)1948 DOI: 10.1039/c3cs60342c
Adam Wilson, Giulio Gasparini and Stefan Matile	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Covalent organic framework	☞Class of porous crystalline polymers ☞Composed of light-weight elements ☞Constructed via strong covalent bonds	Dyn Cov Chem
KeyLrn_Bits	▪ Porphyrin ▪ Phthalocyanine	▪ Catalysis ▪ Optoelectronic devices

Rev* Highlights	
Earlier research	▪ Summarised
2D porphyrin- or phthalocyanine-based COFs	▪ Highlighted Synthesis Through Dynamic Covalent Reactions ▪ Potential Applications
Dynamic covalent chemistry	Leads to Formation of Covalent Bonds With o Error Checking o Proof-Reading

Two-dimensional porphyrin- and phthalocyanine-based covalent organic frameworks	Chinese Chemical Letters, 27(2016)1376-1382 doi.org/10.1016/j.cclet.2016.05.020
Hongmin Wang and Huimin Ding and Xiangshi Meng and Cheng Wang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Tut Rev		Dyn. Cov.Chem

Highlights rev		- Dynamic covalent reactions --Different varities
		- Thermodynamically controlled process – their Characteristic features
		- Applications
		  o Organic 2-D and 3-D molecular architectures
		  o Responsive polymers;

Recent advances in dynamic covalent chemistry	Chem. Soc. Rev., 2013 DOI: 10.1039/c3cs60044k
Yinghua Jin, Chao Yu, Ryan J. Denman and Wei Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Tut Rev	Disulfide	Dyn. Cov.Chem
KeyLrn_Bits	- Disulfide exchange reaction -- mechanism and scope - Structural supramolecular chemistry. - Concept of dynamic covalent chemistry -- exploration - Equilibria of reversible disulfide reactions -- sensitivity to weak non-covalent interactions, - Several non-covalent interactions acting in concert → outcome of structural and constitutional systems. - Kinetic as well as thermodynamics effects, → influence reaction pathways → lead to unexpected products	

	- Hydrophobic effects
	- Interactions
	  ! Cation–π
	  ! Hydrogen bonding
	  ! Aromatic donor–acceptor
	  ! Metal–ligand
		- In dynamic disulfide chemistry

Disulfide exchange: exposing supramolecular reactivity through dynamic covalent chemistry	Chem. Soc. Rev,(2013) DOI: 10.1039/c3cs60326a
Samuel P. Black, Jeremy K. M. Sanders and Artur R. Stefankiewicz	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Rev	Stable radical species	Dyn. Cov.Bonds

Dynamic covalent bonds: approaches from stable radical species	Mater. Chem. Front., 2019, 3, 2270 DOI: 10.1039/c9qm00488b
Daisuke Sakamaki, Samrat Ghosh and Shu Seki	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

DCB-122		
MIni rev	Polymeric materials	Dyn. Cov.Bonds
Highlights Rev*	☞ Powerful dcbs ☞ "click" reactions ☞ Challenges ☞ Potential future developments	☞ Powerful materials that can result from these bonds

Dynamic Covalent Bonds in Polymeric Materials	Chem. Int. Ed. 10.1002/anie.201813525,
Progyateg Chakma and Dominik Konkolewicz Angew	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Dynamic Covalent Chemistry Principles, Reactions, and Applications (book rev)	Chem. Int. Ed. 57(2018)2 DOI: 10.1002/anie.201801152
Wei Zhang and Yinghua Jin. John Wiley and Sons,	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Kinetic and Thermodynamic Control

Kinetic and Thermodynamic Control in Dynamic Covalent Synthesis	dynamic covalent chemistry Covalent Organic Frameworks
Rev	
Synthesis	Synthesis of increasingly complex cyclooligomers, polymers, and diverse compound libraries

☞ Highlights: Interplay between thermodynamic and kinetic considerations in planning a DCC synthesis. Computational models-- reaction thermodynamics -- moderate success

☞ Future: Robust computational -- To predict product distributions in DCC reactions

Kinetic and Thermodynamic Control in Dynamic Covalent Synthesis	Trends in Chemistry, 2(2020)1043-1051 doi.org/10.1016/j.trechm.2020.09.005
Andrew J. Greenlee and Chloe I. Wendell and Morgan M. Cencer and Summer D. Laffoon and Jeffrey S. Moore	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Modular 4D Printing

Shape-memory polymer Metamaterial	Dyn Cov Bonds
Multifunctional devices	✓ Depend upon challenging complex shapes for their consequent functions
3D printing	✓ Is solution - Limited by the fabrication speed and/or - Material diversity
Digitally controlled 2D-to-3D transformation printing	✓ Advantageous in speed - Accessible shapes are limited - Integration of multiple materials is difficult
4D printing + modular assembly	✓ Step 1: 4D photo-printed structures prepared based on dynamically crosslinked polymers ✓ Step 2: Assembled in a modular fashion by interfacial bond exchange → Complex 3D objects with tailorable multiple materials are consequently produced.

Modular 4D Printing via Interfacial Welding of Digital Light-Controllable Dynamic Covalent Polymer Networks	Matter, 2(2020)1187-1197 doi.org/10.1016/j.matt.2020.01.014
Zizheng Fang and Huijie Song and Yue Zhang and Binjie Jin and Jingjun Wu and Qian Zhao and Tao Xie	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Orth. Dyn. Cov. Reactions

Ortho.Dyn.Cov.Reactions	Chapter	Dyn. Cov.Bond
KeyLrn_Bits	☞ Self-Organization ☞ Supramolecular Chemistry to Constitutional Dynamic Chemistry ☞ Adaptation in Constitutional Dynamic Systems ☞ Multiple Dynamics and Dynamic Networks	

Constitutional Dynamic Chemistry: Bridge from Supramolecular Chemistry to Adaptive Chemistry	Top Curr Chem, 322 (2012)1–32 DOI: 10.1007/128_2011_256
Jean-Marie Lehn	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Ortho.Dyn.Cov Reactions		Dyn. Cov.Bond
KeyLrn_Bits	☞ Switchable orthogonal dynamic covalent chemistry ☞ Combination of the orthogonality + differential reactivity ! Sulfonamides as well as nucleophiles ☞ Opportunities for future ! DCC and systems chemistry endeavors	

Three Switchable Orthogonal Dynamic Covalent Reactions and Complex Networks Based on the Control of Dual Reactivity	J. Org. Chem,2018 DOI: 10.1021/acs.joc.8b01332
Yu Hai, Hanxun Zou, Hebo Ye, and Lei You	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Ortho.Dyn.Cov.Reactions	Rev	Dyn. Cov.Bond
KeyLrn_Bits	! Non covalent interactions	

Orthogonal Dynamic Covalent and Non-covalent Reactions, Chapter 5.	in Dynamic Covalent Chemistry: Principles, Reactions, and Applications, First Edition John Wiley & Sons Ltd (2018)
Dan-Wei Zhang and Zhan-Ting Li	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Self-Assembly Using Alkene/Imine Orthogonal Dynamic Covalent Chemistry and Arylene-Ethynylene Macrocycle/DNA Hybrids	B.S. Tulane University, New Orleans, LA, Ph.D thesis (2016)
Kenji D. Okochi	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Four - Orth. Dyn. Cov. Bonds

		Dyn. Cov.BReac
Dream properties	dynamic covalent reactions ☞ Those react reversibly under identical reaction conditions ☞ Do not exhibit any cross-reactivity ☞ Four reactions in one pot in a simultaneous, ☞ Yet orthogonal fashion. ☞ → ☞ Possibilities for the pre-programmed formation of complex thermodynamic assemblies	

Four Simultaneously Dynamic Covalent Reactions. Experimental Proof of Orthogonality.	J. Am. Chem. Soc.,2016 DOI: 10.1021/jacs.6b04532
Helen M. Seifert, Karina Ramirez Trejo, and Eric Van Anslyn	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Three - Orth. Dyn. Cov. Bonds

Three Dynamic Equilibria	Disulfide ; Imines	Dyn. Cov.Chem
KeyLrn_Bits	☞ Coordination chemistry · ☞ Dynamic combinatorial chemistry ☞ Self-assembly · ☞ Systems chemistry	

Disulfides, Imines, and Metal Coordination within a Single System: Interplay between Three Dynamic Equilibria	Chem. Eur. J. 13(2007)9542-9546 DOI: 10.1002/chem.200701228
Rupam J. Sarma, Sijbren Otto and Jonathan R. Nitschke	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Three dynamic covalent reactions

1) Disulfide exchange under basic conditions
2) Hydrazone exchange under acidic conditions
3) Boronic ester exchange under neutral conditions

! These reactions do not proceed simultaneously

! pH controlled to selectively turn on only one reaction at a time

Zhang, K.D.; Matile, S. Angew. Chemie Int. Ed. 2015, 54, 8980–8983.
Zhang, K.D.; Sakai, N.; Matile, S. Org. Biomol. Chem. 2015, 13, 8687–8694.
Rocard, L.; Berezin, A.; De Leo, F.; Bonifazi, D. Angew. Chemie Int. Ed. 2015, 54, 15739–15743.
Lascano, S.; Zhang, K.-D.; Wehlauch, R.; Gademann, K.; Sakai, N.; Matile, S. Chem. Sci. 2016, 00, 1-5
Wong, C.-H.; Zimmerman, S. C. Chem. Commun. 2013, 49, 1679–1695.

Complex Functional Systems with Three Different Types of Dynamic Covalent Bonds	Angew. Chem. Int. Ed. 2015, 54, 8980 –8983 DOI: 10.1002/anie.201503033+
Kang-Da Zhang and Stefan Matile	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

To demonstrate existence and construction functional systems with three orthogonal dynamic covalent bonds of	disulfides, hydrazones and boronate esters,	Orth. Dyn. Cov. Bonds

The third orthogonal dynamic covalent bond†	Chem. Sci., 7(2016) 4720 DOI: 10.1039/c6sc01133k
Santiago Lascano, Kang-Da Zhang, Robin Wehlauch, Karl Gademann, Naomi Sakai and Stefan Matil	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

chemical recycling

	✓ Sustainable plastics ✓ Chemical recycling ✓ Dynamic polymers	
Synth	Poly(disulfide) polymer natural small molecule, thioctic acid used	Dyn.Cov.Chem
	Mild and complete depolymerization into monomers in diluted alkaline aqueous solution → yields of recovered monomers up to 86%.	

- Dynamic covalent ring-opening polymerization
- Sustainable functional plastics

- Intrinsically recyclable and reconfigurable
- Mechanically robust ionic films
- Self-healing elastomers

Dual closed-loop chemical recycling of synthetic polymers by intrinsically reconfigurable poly(disulfides)	Matter, (2021) doi.org/10.1016/j.matt.2021.01.014
Qi Zhang and Yuanxin Deng and Chen-Yu Shi and Ben L. Feringa and He Tian and Da-Hui Qu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

✓ Imine	✓ Stress relaxation ✓ Stress intensification	Dyn Cov Chem
Reversible covalent bonds + Elastomers with reprocessability and recyclability		
Prep	Small-molecular aldehydes and amines → polyimine elastomer (PIE)	+ with abundant dynamic reversible imine bonds from

Network reconfiguration and unusual stress intensification of a dynamic reversible polyimine elastomer	Polymer, 186(2020)122031 doi.org/10.1016/j.polymer.2019.122031
Yufeng Lei and Shijie Shan and Yaling Lin and Anqiang Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels

Rev		Dyn Cov Bonds
Highlights of Rev - Preparation DCB hydrogels - Developing techniques		Unique prop - Autonomous healing ability - Responsiveness under stimuli

o Materials of DCB hydrogels ☞ Application o Biomedical o Smart materials	

Advances in hydrogels based on dynamic covalent bonding and prospects for its biomedical application	European Polymer Journal,139(2020)110024 doi.org/10.1016/j.eurpolymj.2020.110024
Jing Ye and Shuwen Fu and Shiya Zhou and Mohan Li and Kaiyu Li and Wei Sun and Yinglei Zhai	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Rev	hydrogels	Dyn. Cov.Bonds
Highlights	☞ Dynamic covalent crosslinks ☞ Functional systems ☞ Future developments of dynamic covalent hydrogels	☞ Properties viz. Self-healing, shape memory, stimuli-induced stiffness changes

Dynamic covalent bonds in self-healing, shape memory, and controllable stiffness hydrogels	The Royal Society of Chemistry (2020) DOI: 10.1039/c9py01694e
M. Mario Perera and Neil Ayres	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

🕮 Hydrogels	Dyn Cov Chem	
🕮 Rev	🕮 Highlight: Synthetic biomaterials -- dynamic mechanical properties of soft tissues 🕮 Future: Development and application of viscoelastic biomaterials	
🕮 Mechanobiology Matrix biology	To elucidate 🕮 how the ECM (extracellular matrix) mechanical environment influences cell fate and function o both in vitro and in vivo	
KeyLrn_Bits	▪ Biomaterials ▪ Viscoelasticity,	▪ Covalent adaptable networks ▪ Mechanotransduction

Dynamic covalent hydrogels as biomaterials to mimic the viscoelasticity of soft tissues	Progress in Materials Science, (2020)100738 doi.org/10.1016/j.pmatsci.2020.100738
Shengchang Tang and Benjamin M. Richardson and Kristi S. Anseth	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

🕮 Hydrogel.Adaptable	Dyn Cov Chem	
KeyLrn_Bits	✓ Dyn mech microenvironment ✓ Supramolecular chemistry	✓ Yes-associated protein ✓ Regenerative medicine
Hydrogels	- Three-dimensional platforms - Serve as substitutes for native extracellular matrix.	

regenerative medicine	🕮 Hydrogels play keyrole due to similarities to native matrix in water content and flexibility
Highlights of Rev	🕮 Strategies to design adaptable hydrogel network with reversible linkages ▪ Based on knowledge of supramolecular chemistry and dynamic covalent chemistry 🕮 Mechanism of dynamic mechanical microenvironment 🕮 Influences on and of cell behaviors and fate 🕮 State-of-knowledge of bioprinting 🕮 Limitations and challenges for adaptable hydrogel 🕮 Perspectives for future research and goals

Adaptable hydrogel with reversible linkages for regenerative medicine: Dynamic mechanical microenvironment for cells	Bioactive Materials, 6(2021)1375-1387 doi.org/10.1016/j.bioactmat.2020.10.029
Zongrui Tong and Lulu Jin and Joaquim Miguel Oliveira and Rui L. Reis and Qi Zhong and Zhengwei Mao and Changyou Gao	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogel.Adaptable		Dyn Cov Chem
KeyLrn_Bits	✓ Adaptable polymer networks ✓ Soft matter	✓ Polymer engineering ✓ Biomedical material
Thermosets & thermoplastics	- limited by the static materials properties	
Highlights of Rev	🕮 Design of dynamic covalent networks 🕮 Gels using boronic ester cross-links. 🕮 Boronic ester chemistry –influence of synthetic modifications 🕮 Influence of network topology& connectivity on ! Macroscale properties of the assembled networks	
Future scenario	🕮 Todays design principles → will aid 🕮 Fabrication of next-generation boronic ester-based biomaterials	

Design of moldable hydrogels for biomedical applications using dynamic covalent boronic esters	Materials Today Chemistry, 12(2019)16-33 doi.org/10.1016/j.mtchem.2018.12.001
B. Marco-Dufort and M.W. Tibbitt	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels,		Dyn Cov Chem
KeyLrn_Bits	☞ Stimuli-responsive polymers ☞ Smart polymers ☞ Stimuli-responsive materials	+ Drug delivery, + Controlled release
☞ Stimuli-responsive polymers for	☞ Changes in pH ☞ Temperature ☞ Electrolyte concentration	🕮 Thiol-responsive 🕮 Redox-responsive polymers

Future perspectives and recent advances in stimuli-responsive materials	Progress in Polymer Science, 35(2010)278-301 doi.org/10.1016/j.progpolymsci.2009.10.008
Debashish Roy and Jennifer N. Cambre and Brent S. Sumerlin	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels Adaptable Elastin-like protein-hyaluronic acid (ELP-HA)		Dyn Cov Chem
KeyLrn_Bits	▪ Chemical recycle ▪ Sustainable, plastics	▪ Ring-opening polymerization ▪ Depolymerization, ▪ Polythioester

Dynamic covalent chemistry

- Goal: To access infinitely recyclable plastics
- Approach: to design thermodynamically neutral systems based on dynamic covalent bond,
- Ex: synthesis of polythioesters PNR-PenTE with tailored properties
  - From penicillamine-derived β-thiolactones and
  - Depolymerization under mild conditions

☞ Mechanism : The gem-dimethyl group adjusts the thermodynamics of (de)polymerization to near equilibrium,
  - Confers better (de)polymerization control by reducing the activity and conformational possibilities of the chain-end thiolate groups,
  - stabilizes the thioester linkages in the polymer backbone

Geminal Dimethyl Substitution Enables Controlled Polymerization of Penicillamine-Derived β-Thiolactones and Reversed Depolymerization	Chem, 6(2020)1831-1843 doi.org/10.1016/j.chempr.2020.06.003
Wei Xiong and Wenying Chang and Dong Shi and Lijiang Yang and Ziyou Tian and Hao Wang and Zhengchu Zhang and Xuhao Zhou and Er-Qiang Chen and Hua Lu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

o Gels ✓ Supramolecular gels, ✓ Molecular gels, o Materials ✓ Porous	Dyn Cov Chem
☞ To understand the dynamic covalent bonding	o Dynamic covalent cross-linked polymers -- - act as gelators o Illustrate structure–property relationships of these dynamic covalent gels
Highlights of rev	☞ Dynamic covalent reactions used in gels from small molecules ☞ Structure–property relationships in dynamic covalent gels ☞ Sets of dynamic covalent gels based on ✓ Nature of gelators ✓ Interactions between gelators

Dynamic covalent gels assembled from small molecules: from discrete gelators to dynamic covalent polymers	Chinese Chemical Letters, 28(2017)168-183 doi.org/10.1016/j.cclet.2016.07.015
Jian-Yong Zhang and Li-Hua Zeng and Juan Feng	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Gels; nanoparticles		Dyn. Cov.Chem
KeyLrn_Bits	☞ Polymers ☞ Responsive materials	☞ Self-healing materials

Dynamic Covalent Polymers	Journal of polymer science, part a: polymer chemistry,54(2016)3551–3577 DOI: 10.1002/pola.28260
Fatima Garcia, Maarten M. J. Smulders	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogel	Rev	Dyn. Cov.Bond
ghts Rev*	✓ Schiff base ✓ Click chemistry	✓ Self-healing; ✓ Tissue engineering
	biomedical applications of hydrogels	
	✓ Drug delivery ✓ Tissue regeneration ✓ Wound healing	✓ Tissue adhesives ✓ Bioprinting ✓ biosensors ✓
	✓ Design and preparation of hydrogels based on various types of Schi base linkages	

Hydrogels Based on Schi Base Linkages for Biomedical Applications	Molecules, 24(2019)3005; doi:10.3390/molecules24163005
Junpeng Xu, Yi Liu and Shan-hui Hsu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dyn. Cov.Bonds
Dream properties		☞ Excellent mechanical properties ☞ Remarkable self-healing ability

Ultrastretchable, Self-Healable Hydrogels Based on Dynamic Covalent Bonding and Triblock Copolymer Micellization	Peng Wang, Guohua Deng, Lanying Zhou, Zhiyong Li, and Yongming Chen ACS Macro Lett. 2017, 6, 881−886 DOI: 10.1021/acsmacrolett.7b00519

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dyn boronic ester bonds
Glucose-responsive hydrogels Prep	3-acrylamidophenyl boronic acid copolymerized with 2-lactobionamidoethyl methacrylate (p(APBA-b-LAMA))	+ Rapid increase in equilibrium of swelling, which was up to 1856% after incubation with aqueous solution

A glucose-sensitive block glycopolymer hydrogel based on dynamic boronic ester bonds for insulin delivery	Carbohydrate Research, 445(2017)32-39 doi.org/10.1016/j.carres.2017.04.006
Baoqi Cai and Yanping Luo and Qianqian Guo and Xinge Zhang and Zhongming Wu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels	Multi-responsiveness Injectability Drug carriers	Dyn Cov Bonds
Prep	Mixing of DMA-stat-2APBA + (OH)2-PDMA-b-PNIPAM diblock copolymers in PBS (pH 7.4) solution at temperature, i.e. 37 °C	Multiple stimuli-responsiveness ▪ pH ▪ Temperature ▪ Glucose redox reaction ▪ Mechanical field

Injectable multi-responsive hydrogels cross-linked by responsive macromolecular micelles	Reactive and Functional Polymers, 161(2021)104866 doi.org/10.1016/j.reactfunctpolym.2021.104866
Yong Gao and Amin Deng and Xionghui Wu and Changsheng Sun and Chenze Qi	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels Injectable	Self-healing	Dyn Cov Bonds
Prep	Aldehyde functionalized hyaluronic acid (HA-CHO) + disulfide containing crosslinker - 3,3′-dithiobis(propionic hydrazide) (DTPH)	Multiple responsive properties 🕮 Strain 🕮 Reduction 🕮 Oxidation 🕮 Enzyme U
Tissue adhesives of yester years	- Cannot meet the requirements of sophisticated surgeries	**New hydrogel** 🕮 much high lap shear adhesive strength (up to 120 kPa) to the porcine skin, which surpasses 65.8% to BioGlue V

An injectable multi-responsive hydrogel as self-healable and on-demand dissolution tissue adhesive	Applied Materials Today, 22(2021)100967 doi.org/10.1016/j.apmt.2021.100967
Sigen A and Qian Xu and Melissa Johnson and Jack Creagh-Flynn and Manon Venet and Dezhong Zhou and Irene Lara-Sáez and Hongyun Tai and Wenxin Wang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Rev	o Reversible polymer o Stimulus-responsive polymer o Exchange reaction	Dyn. Cov. Bonds Dyn.Comb.Chem
High lights of Rev		
☞ Dyn. Cov. Bonds [C Nbonds in imine derivatives and C Obonds in alkoxyamine] impact on ☞ Reactive polymer blends ☞ Ring–chain equilibrium ☞ Reorganizable polymers and polymeric systems ☞ Dynamic smart polymer materials can reform their structures and constitutions ☞ Intelligent systems using equilibrium under reorganization processes and stimulus-responsive polymeric materials based on bond-reformation		

Dynamic covalent polymers: Reorganizable polymers with dynamic covalent bonds	Progress in Polymer Science, 34 (2009)581-604 doi.org/10.1016/j.progpolymsci.2009.03.001
Takeshi Maeda and Hideyuki Otsuka and Atsushi Takahara	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Prep chiral hydrogels	✓ Homogeneous mixture of chitosan + betulinic aldehyde in different molar ratios ✓ Under the effect of ultrasound	Dyn Comb Chem

Chiral betulin-imino-chitosan hydrogels by dynamic covalent sonochemistry	Ultrasonics Sonochemistry, 45(2018)238-247 doi.org/10.1016/j.ultsonch.2018.03.022
Manuela Maria Iftime and Luminita Marin	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels	✓ Native protein ✓ Cytochrome C, Boronic acid, Hydrogel ✓ Bioactive ✓ Responsive	Dyn Cov Interactions Dyn Boronic Acid Chem	
Appl:	✓ Controlled administration	Prop:	Attractive rheological properties
In vivo	☞ Upon acidification o Hydrogel matrix dissociated o Release active enzymes into A549 cells, which initiates apoptosis		

Native protein hydrogels by dynamic boronic acid chemistry	Tetrahedron, 73(2017) 4979-4987 doi.org/10.1016/j.tet.2017.06.066
Christiane Seidler and David Y.W. Ng and TanjaWeil	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels	Dynamic hyaluronic acid-based	Dyn. Cov. Bonds
Appl biomedical	Responsive drug delivery system + Self-healing + Anti-oxidative + ROS responsive drug delivery	
	+ Bio-inks for ✓ 3D printing/bioprinting	
Prep	Phenylboronic acid modified hyaluronic acid (HA-PBA) and the commercially available poly (vinyl alcohol) (PVA)	
+ Injectability + Self-healing	☞ Basis: dynamic bond	

Fabrication of versatile dynamic hyaluronic acid-based hydrogels	Carbohydrate Polymers, 233(2020)115803 doi.org/10.1016/j.carbpol.2019.115803
Wen Shi and Blake Hass and Mitchell A. Kuss and Haipeng Zhang and Sangjin Ryu and Dongze Zhang and Tieshi Li and Yu-long Li and Bin Duan	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogels Adaptable Elastin-like protein-hyaluronic acid (ELP-HA)		Dyn Cov Chem
KeyLrn_Bits	▪ Cartilage regeneration	▪
Prep	reaction between hydrazine-modified ELP + aldehyde-modified HA	+ dynamic hydrazone bonds →
Appl	☞ 3D scaffolds with decoupled niche properties ➔ to guide other desirable cell fates and tissue repair	

Elastin-like protein-hyaluronic acid (ELP-HA) hydrogels with decoupled mechanical and biochemical cues for cartilage regeneration	Biomaterials, 127(2017)132-140 doi.org/10.1016/j.biomaterials.2017.02.010
Danqing Zhu and Huiyuan Wang and Pavin Trinh and Sarah C. Heilshorn and Fan Yang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

🕮 Hydrogels	Dyn Cov Bonds Rev
🕮 Drug delivery, 🕮 Tissue engineering	Requirements ✓ Favorable carrier property in three-dimension ✓ Biocompatibility ✓ Low invasive ✓ Adaptable shape for administration

Recent advances of injectable hydrogels for drug delivery and tissue engineering applications	Polymer Testing, 81(2020)106283 doi.org/10.1016/j.polymertesting.2019.106283
Yining Sun and Ding Nan and Haiqiang Jin and Xiaozhong Qu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Natural protein hydrogels - Exhibit poor mechanical properties	+ High strength	dynamic covalent chemistry
Synthesis	☞ Tetrakis(hydroxymethyl)phosphonium chloride (THPC) cross-linked BSA (THPC-BSA) as dynamic covalent bond cross-linked first network ☞ Covalently cross-linked polyacrylamide (PAAM) as second network	
Prop	+ Excellent tensile properties + Displayed extremely fast self-recovery property and fatigue resistance. + Double network, Hybrid + Self-recovable	

Natural protein-based hydrogels with high strength and rapid self-recovery	International Journal of Biological Macromolecules, 141(2019)108-116 doi.org/10.1016/j.ijbiomac.2019.08.258
Zhao Liu and Ziqing Tang and Lin Zhu and Shaoping Lu and Feng Chen and Cheng Tang and Huan Sun and Jia Yang and Gang Qin and Qiang Chen	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

🕮 Inorganic-organic hybrid gels	Dyn Cov Bond
Prep	radical exchange reaction:TiO2 nanoparticles modified with organophosphonic acid bearing C-ON bonds
	The modification of TiO2 with N-tert-butyl-N-(1-dihydroxyphosphoryl-2,2-dimetylpropyl)- aminoxymethyl benzene (DEPN-BA) + isodecyl phosphonic acid (IDP)

Preparation of inorganic-organic hybrid gels by radical exchange reaction using TiO2 nanoparticles modified with organophosphonic acid bearing C-ON bonds	Materials Today: Proceedings, 16(2019)180-186 doi.org/10.1016/j.matpr.2019.05.291
Kohei Kaneta and Seiichi Tahara and Naokazu Idota and Yoshiyuki Sugahara	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Hydrogel.	Dyn Cov Chem	
KeyLrn_Bits	✓ Chitosan ✓ Nitrosalicylaldehyde,	✓ Biocompatibility ✓ Antitumor functionality

Prep of ☞ Hydrogels based on ☞ Chitosan polyamine ☞ Nitrosalicylaldehyde	by 🕮 Dynamic covalent chemistry 🕮 Imination 🕮 Transimination reactions towards → ordered clusters
Hydrogelation mechanism	🕮 Mechanical properties o Rheological measurements

🕮 NMR 🕮 FTIR spectroscopy 🕮 X-ray diffraction polarized light microscopy	🕮 Morphology o Electron scanning microscopy→ hydrogels exhibited a channels microstructure

🕮 Cytotoxicity in vitro o on HeLa cancer cells o Result : favorable	🕮 Biocompatibility was monitored in vivo o by subcutaneous implantation on rats o Result : favorable
🕮 Future prospects	🕮 Local therapy on human patients 🕮 Tumour 🕮 Cancer

Biocompatible chitosan based hydrogels for potential application in local tumour therapy	Carbohydrate Polymers, 179(2018) 59-70 doi.org/10.1016/j.carbpol.2017.09.066
Anda-Mihaela Olaru and Luminita Marin and Simona Morariu and Gabriela Pricope and Mariana Pinteala and Liliana Tartau-Mititelu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Human Health
Medicinometrics

drug delivery systems

☞ Cancer therapy ☞ Stimuli-liable properties ☞ Regulating the drug release kinetics		Dyn Cov Chem
Highlights of Rev	☞ Major classes of dynamic covalent bonds ☞ Responsive mechanisms ☞ Acid-activatable ☞ Reduction-activatable	☞ Combination strategies of dual dynamic covalent bonds ☞ Impact on complex tumor microenvironment
	☞ Drug Deliv Syst ☞ Tumor-targeted	☞ Future prospects of Dyn Cov Chem in DDSs
☞ Drug delivery systems	Intended to ☞ Deliver drugs at the intended targets ☞ Tumor cells or tissue	Mechanism ☞ Prolonging blood circulation ☞ Optimizing pharmaceutical profiles

- Therapeutic efficacy of DDSs severely impaired by insufficient or non-specific drug release
  - ! Remedy: DDSs having Dyn Cov Bonds with stimuli-liable property
    - ▪ Regulate drug release kinetics

Dynamic covalent chemistry-regulated stimuli-activatable drug delivery systems for improved cancer therapy	Chinese Chemical Letters, 31(2020) 1051-1059 doi.org/10.1016/j.cclet.2019.12.002
Qiwen Zhu and Madiha Saeed and Rundi Song and Tao Sun and Chen Jiang and Haijun Yu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

tumor therapy

Intracellular switch on/off controlled release .	Dyn Cov Bonds	
KeyLrn_Bits	✓ Bioreduction-rupture, PEI-1.8 kDa ✓ Lysosomal escape ✓ Reduction-sensitive	✓ siRNA delivery ✓ siRNA switch on/off controlled release
Nanogel with Dynamic covalent bond crosslinked prepred	←← By thiolated PEI of 1.8 kDa(PEI-1.8 kDa) and biodegradable dextrin	

Bioreduction-ruptured nanogel for switch on/off release of Bcl2 siRNA in breast tumor therapy	Journal of Controlled Release, 292(2018)78-90 doi.org/10.1016/j.jconrel.2018.02.036
Huipeng Li and Xue Yang and Fang Gao and Chenggen Qian and Chenzi Li and David Oupicky and Minjie Sun	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Anti-recurrence/metastasis and chemosensitization therapy with thioredoxin reductase-interfering drug delivery system	Biomaterials, 249(2020)120054 doi.org/10.1016/j.biomaterials.2020.120054
Jichun Yang and Shuojiong Pan and Shiqian Gao and Yiheng Dai and Huaping Xu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

dental restorative

Imines	Dyn Cov Bond
KeyLrn_Bits	▪ Adaptive interface, Interfacial stress relaxation
Dental restorative composites Limitations	- Stress induced microcracks from polymerization shrinkage, thermal and other stresses along with the low fracture toughness of methacrylate-based composites remain significant problems
DCC at the resin–filler interface	➔ Stress-relieving mechanism operative in dental restorative materials

Dynamic covalent chemistry (DCC) in dental restorative materials: Implementation of a DCC-based adaptive interface (AI) at the resin–filler interface for improved performance	Dental Materials, 36(2020)53-59 doi.org/10.1016/j.dental.2019.11.021
Nancy Sowan and Adam Dobson and Maciej Podgorski and Christopher N. Bowman	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Healing

☞ Repair	☞ Self Repair
☞ Healing	☞ Auto-healing
	☞ Rehealing
	☞ Self-healable

Self-healing

		Dyn. Cov. Chem
Hydrogel	Nanocomposite DNA-based hydrogel crosslinked with oxidized alginate (oa) via the formation of reversible imine linkages	
Properties	Self-healing ; shear-thinning	
	Reversible covalent imine bonds Formed between the aldehyde groups of OA and the amine groups of DNA nucleotides	
	Sustained drug release --simvastatin for more than a week	

Self-healing DNA-based injectable hydrogels with reversible covalent linkages for controlled drug delivery	Acta Biomaterialia, 105(2020)159-169 doi.org/10.1016/j.actbio.2020.01.021
Sayantani Basu and Settimio Pacelli and Arghya Paul	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dyn. Cov. Bonds
Hydrogel	Highly stretchable and tough gel	cyclodextrin + polyacrylamide azobenzene alginate-based
Self-healing properties	✓ Irradiation upon ultraviolet light /visible light → Reversible transformation of the sol-gel ✓ Basis: host-guest interaction between cyclodextrin and azobenzene	
	The recovery gel elongation at 48 h healing in the dark condition was is 0.04 MPa, with an elongation of 1140 %.	

Highly stretchable and tough alginate-based cyclodextrin/Azo-polyacrylamide interpenetrating network hydrogel with self-healing properties	Carbohydrate Polymers, 256 (2021)117595 doi.org/10.1016/j.carbpol.2020.117595
Furui He and Longzheng Wang and Shujuan Yang and Wenqi Qin and Yuhong Feng and Yuanyuan Liu and Yang Zhou and Gaobo Yu and Jiacheng Li	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Polymers	Dyn Cov Bonds
Proc: ☞ Schiff base from cystine and vanillin ☞ 1,4-butanediol (BD) to ensure miscibility with polyurethane (PU) ☞ PU crosslinked with the Schiff base → SPU	Prop o Self-healing o Dual-responsive (heat and uv irradiation) o Recyclability

Self-healing of cross-linked PU via dual-dynamic covalent bonds of a Schiff base from cystine and vanillin	Materials & Design, 172(2019)107774 doi.org/10.1016/j.matdes.2019.107774
Sang-Hyub Lee and Se-Ra Shin and Dai-Soo Lee	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dynamic Covalent Bonds Mobile Covalent Bonds
Self-healing material	Prepared by combining the mobility of a polyrotaxane with the versatility of dynamic covalent chemistry	Basis: Combination of physical (conformational changes) + chemical (bond reformation) phenomena

Combining Mobile and Dynamic Bonds for Rapid and Efficient Self-Healing Materials	Chem, 1(2016)672-673 doi.org/10.1016/j.chempr.2016.10.013
Guillaume De Bo	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dynamic Covalent Bonds
Self-healing	Polymer	☞ Crack-healing capability
Prep	Dynamic polymer networks	Dynamic bonds: o Dynamic covalent bond ▪ Hydrogen bond ▪ Ionic bond ▪ Metal-ligand coordination ▪ Hydrophobic interaction
Self-healing process theory	✓ Polymer chains diffuse across the interface to reform the dynamic bonds, ✓ It is modeled by a diffusion-reaction theory. which predict the stress-stretch behaviors of original and self-healed DPNs	

Mechanics of self-healing polymer networks crosslinked by dynamic bonds	Journal of the Mechanics and Physics of Solids, 121(2018)409-431 doi.org/10.1016/j.jmps.2018.08.007
Kunhao Yu and An Xin and Qiming Wang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Chap 2: Rev	Dyn. Cov. Bonds	
Self-healing polymer materials	Advantages + Minimization of system breakdown + Decrease in the cost of maintenance	+ Increased working life + Increased safety index
Chemistries of self-healing systems	+ Irreversible covalent bond formation via extrinsic microcapsules self-healing process + Reversible dynamic covalent chemistry .	+ Reversible supramolecular interactions to improve the multiple healing times + through intrinsic self-healing process

Appl	☞ Biomaterials ☞ Bioelectronics ☞ Sensors/ actuators ☞ Coating paints technologies	☞ Electronics ☞ Energy devices such as membranes ☞ 3D/4D Printing ☞ Tissue engineering ☞ Soft robotics skin

Chapter 2 - Types of chemistries involved in self-healing polymeric systems	Self-Healing Polymer-Based Systems, Elsevier(2020)17-73 doi.org/10.1016/B978-0-12-818450-9.00002-7
Anil K. Padhan and Debaprasad Mandal	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dynamic Covalent Bonds
Self-healing Recyclable	Rubber composites	☞ Thermorevesible ☞ thermal reprocessability
KeyLrn_Bits	▪ Elastomer\ ▪ Thermorevesible bonding	▪ Reprocessability
Prep	Ethylene propylene diene monomer (EPDM) rubber grafted with maleic anhydride (EPDM-g-MA) → thermoreversibly crosslinked by silane modified silica	▪ Rubber network could be broken at high temperature ▪ reconstructed by thermal annealing,

Recyclable and self-healing rubber composites based on thermorevesible dynamic covalent bonding	Composites Part A: Applied Science and Manufacturing, 129(2020)105709 doi.org/10.1016/j.compositesa.2019.105709
Zhixin Jia and Shuli Zhu and Yongjun Chen and Wenqiang Zhang and Bangchao Zhong and Demin Jia	

Self-healing		Dynamic Covalent Bonds
KeyLrn_Bits	▪ Anion exchange membrane, ▪ Diels-Alder reaction,	▪ Organic aqueous redox flow battery
Synth	▪ Block copolymer from o Vinylbenzyl chloride +2-((4-vinylbenzyloxy) methyl) furan by RAFT polymerization o By solution casting and reacting at 80 °C, an AEM (Anion exchange membranes) with dynamic network was prepared.	
	✓ AEM has a Cl− conductivity of 32.7 mS cm−1 at 80 °C + Man-made cracks on the membrane can be self-healed	

Self-healing anion exchange membrane for pH7 redox flow batteries	Chemical Engineering Science, 201(2019)167-174 doi.org/10.1016/j.ces.2019.02.033
Jianqiu Hou and Yahua Liu and Yazhi Liu and Liang Wu and Zhengjin Yang and Tongwen Xu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Self-healing, Injectable		Dynamic Covalent Chem
KeyLrn_Bits	▪ CAN	▪ Dissociative exchange
Compd	o Aromatic thiourethane, Polythiourethane	
S-aromatic polythiourethane (PTU) networks	linkage is a promising dynamic covalent bond ➔ Responsible for self-healable, injectable and recyclable materials	
Covalent adaptable networks (CAN)	✓ Are polymer systems ✓ Crosslinks can undergo reversible rearrangement reactions.	
	✓ The stimuli-triggered dynamism of the network enables + Healing + Reprocessing of pristine materials + Without damaging their original mechanical properties	

New injectable and self-healable thermoset polythiourethane based on S-aromatic thiourethane dissociative exchange mechanism	Polymer, 196(2020)122461 doi.org/10.1016/j.polymer.2020.122461
A. Erice and A. Ruiz de Luzuriaga} and I. Azcune and M. Fernandez and I. Calafel and H.-J. Grande and A. Rekondo	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Acrylate elastomers, Click chemistry, Disulfide bonds	Dynamic Covalent Chem
Compd	Synthesized thiol-ene click reactions between acrylate monomers and polysulfide oligomers → Novel kind of acrylate-based elastomers with exchangeable disulfide crosslinks by
restoration of mechanical properties	Base system itself without the extra addition of self-healing catalyst + Mechanical properties of acrylate-based elastomers restored more than 90% with a habitation of 5 h.

Self-healable and reprocessable acrylate-based elastomers with exchangeable disulfide crosslinks by thiol-ene click chemistry	Polymer, 212(2021)123132 doi.org/10.1016/j.polymer.2020.123132
Hong Gao and Yingchun Sun and Miaomiao Wang and Bo Wu and Guoqiang Han and Ling Jin and Kui Zhang and Youyi Xia	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Rehealing behavior		Dynamic Covalent Bond Thiol-Michael bond
KeyLrn_Bits	▪ Polyester network	▪ Michael addition polymerization
Rehealing time	Increasing the curing temperature to 120 °C led to a decrease in time to reheal (≤8 h),	
	+	

Probing the dynamic and rehealing behavior of crosslinked polyester networks containing thermoreversible thiol-Michael bonds	Polymer, 145(2018) 286-293 doi.org/10.1016/j.polymer.2018.05.009
Samantha P. Daymon and Kevin M. Miller	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Monomers → Polymers

☞ Polymers
☞ Wormlike micelles
☞ Foldamers
☞ Vitrimers

wormlike micelles

CTAB/CB/NA		Dyn Cov Bonds
Prep	Cationic surfactant cetyltrimethylammonium bromide (CTAB) 4-carboxybenzaldehyde (CB) aniline (NA) molar ratio of 60:40:40 (CTAB/CB/NA)→ ternary composite fluid state transition system	
Inst analysis	☞ Bottle test method	☞ Infrared spectroscopy

	Rheology	1H NMR Cryo-TEM
Information	If pH increased from 3.13 to 7.25, CTAB/CB/NA solution changed from a low-viscosity fluid to a transparent gel-like fluid [viscosity increased from 1 to 4.6 × 104 mPa·s] If pH decreased Viscosity recovered	
Expl	drastic change in rheological properties is due to pH dependent ionization and formation of dynamic covalent bond CBNA Reason: Morphology of micelles system changes from spherical to worm-like micelles	

Compd	Worm-like micelles	Property	Rheological
State	Fluid	Response	pH

Fluid state transition mechanism of a ternary component aqueous solution based on dynamic covalent bond	Journal of Molecular Liquids, 332(2021)115849 doi.org/10.1016/j.molliq.2021.115849
Menglan Li and Wanli Kang and Zhe Li and Hongbin Yang and Xin Kang and Ruxue Jia and Anqing Xie and Bauyrzhan Sarsenbekuly and Maratbek Gabdullin	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

wormlike micelles		Dyn Cov Bond
KeyLrn_Bits	Phase transfer	Hydrotrope
single stimuli for switch on and off the viscoelasticity of WLMs	pH, CO_2 Temperature	Light Redox and magnetic fields
Prep	cetyltrimethylammonium bromide (CTAB) + 4-formylbenzoic acid (FA) + hexylamine (HA) at the molar ratio of 60:25:25	
Rheological parameter	Increased from ~1.1 mPa·s to ~68,000 as pH increase from 6.01 to 12.07 i.e. transitions from a water-like fluid → viscoelastic fluid → gel-like solution o Reversed by decreasing pH from alkaline to acidic	

Responsive wormlike micelle with pH-induced transition of hydrotrope based on dynamic covalent bond	Journal of Molecular Liquids, 86(2019) 110935 doi.org/10.1016/j.molliq.2019.110935
Pengxiang Wang and Tongyu Zhu and Xiaoyu Hou and Yilu Zhao and Xiangfeng Zhang and Tongyu Wang and Hongbin Yang and Wanli Kang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Polymers

☞ Polymer reactions ☞ Cross-linking		Dyn.Cov.Chem
synth	☞ Low-Tg polymers with alkoxyamine units in the side chains	🕮 By radical copolymerisation of 2-ethylhexyl acrylate and two kinds of alkoxyamine-containing acrylate monomers
Structural transition between low-Tg linear polymers and cross-linked polymers	Spectroscopy ☞ 1H and 13C NMR, ☞ Fourier transform infrared	Measurement 🕮 Rheology 🕮 Swelling experiment 🕮 Gel permeation chromatography
o transition from a liquid-like flowable polymer state → to a rubber-like polymer state was confirmed		

Reversible cross-linking reactions of alkoxyamine-appended polymers under bulk conditions for transition between flow and rubber-like states	Polymer, 55(2014)1474-1480 doi.org/10.1016/j.polymer.2014.01.055
Jing Su and Yoshifumi Amamoto and Tomoya Sato and Masashi Kume and Taro Inada and Tomoyuki Ohishi and Yuji Higaki and Atsushi Takahara and Hideyuki Otsuka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

✓ Olefin metathesis	Dyn Cov Chem
Synthesis of linear polyethylene/polyester copolymers	✓ Produced by olefin cross metathesis ✓ Catalytic hydrogenation ✓

Synthesis of polyethylene/polyester copolymers through main chain exchange reactions via olefin metathesis	Polymer, 55(2014)6245-6251 doi.org/10.1016/j.polymer.2014.10.001
Takeshi Maeda and Shigehisa Kamimura and Tomoyuki Ohishi and Atsushi Takahara and Hideyuki Otsuka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Compd	Polymer molecules	self-healing	Dyn Cov Bonds
Rev	Reaction conditions mechanisms of different types of DCBs Existing challenges and future development directions		
Appl	tissue adhesives, tissue egeneration	drug delivery, sensors	3D printing, fluorescent probes coatings

An overview of dynamic covalent bonds in polymer material and their applications	European Polymer Journal, 141(2020)110094 doi.org/10.1016/j.eurpolymj.2020.110094
Shuo Huang and Xin Kong and Yingshuo Xiong and Xiaoran Zhang and Hao Chen and Wenqing Jiang and Yuzhong Niu and Wenlong Xu and Chunguang Ren	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Foldamer	Bipyridinium	Dyn Cov Chem
KeyLrn_Bits	▪ Donor–acceptor interaction	▪ Conjugated radical cation dimerization

Pleated polymeric foldamers driven by donor–acceptor interaction and conjugated radical cation dimerization	Chinese Chemical Letters, 27(2016)817-821 doi.org/10.1016/j.cclet.2016.03.041
Yun-Chang Zhang and Lan Chen and Hui Wang and Ya-Ming Zhou and Dan-Wei Zhang and Zhan-Ting Li	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Rev		Dyn Cov Chem
KeyLrn_Bits	▪ Reversible covalent polymers ▪ Application	▪ Polymer engineering, ▪ Adaptivities
Rev Highlights	🕮 Theoretical and experimental achievements 🕮 Design and preparation of materials through 🕮 Basis of reversible covalent chemistry 🕮 Rheology of reversible covalent polymers, 🕮 Methods of construction of reversible covalent polymers, 🕮 Smart, adaptive properties offered by reversible covalent chemistry.	
	🕮 Advantages and weaknesses of representative reaction systems 🕮 Challenges and opportunities to engineering	

Polymer engineering based on reversible covalent chemistry: A promising innovative pathway towards new materials and new functionalities	Progress in Polymer Science, 80(2018)39-93 doi.org/10.1016/j.progpolymsci.2018.03.002
Ze Ping Zhang and Min Zhi Rong and Ming Qiu Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Modular approach for theranostic polymer conjugates with activatable fluorescence: Impact of linker design on the stimuli-induced release of doxorubicin	Journal of Controlled Release, 285(2018)200-211 doi.org/10.1016/j.jconrel.2018.07.015
Gregor Nagel and Harald R. Tschiche and Stefanie Wedepohl and Marcelo Calderón	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Vitrimers

☞ Vitrimer	☞ Recyclable ☞ Tunable	Dyn Cov Chem

Recyclable ethylene-vinyl acetate copolymer vitrimer foams	Polymer,(2021)123662 doi.org/10.1016/j.polymer.2021.123662
Lin Cheng and Sijun Liu and Wei Yu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dyn. Cov. Bond.Exchange
Epoxy vitrimer	Fully bio-based	
Synth	ESO (Epoxidized soybean oil) + rosin derivative-fumaropimaric acid (FPA)	
Properties	Tg (glass transition temperature):65 °C	Tensile strength :16 MPa
	Self-healing, triple-shape memory and reprocessing	

A fully bio-based epoxy vitrimer: Self-healing, triple-shape memory and reprocessing triggered by dynamic covalent bond exchange	Materials & Design, 186(2020) doi.org/10.1016/j.matdes.2019.108248

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Dynamic network topology	Polymer network	dyn. Cov. Bonds.chem
Trend Rev synapsis	o Concept of vitrimers o Most unique properties o Outstanding challenges o Recyclable high performance materials	
➔ Recyclability ➔ Processability ➔ Self-Healing ➔ Adhesion	+ Low cost + Desirable physical properties	
Vitrimers. Def.	Permanent networks of polymer chains connected via dynamic covalent bonds	
	+ Allow the network to change its topology + Maintain a constant number of chemical bonds at all temperatures.	

Vitrimers: Permanently crosslinked polymers with dynamic network topology	Progress in Polymer Science, 104 (2020) 101233 doi.org/10.1016/j.progpolymsci.2020.101233
Nathan J. Van Zee} and Renaud Nicolaÿ	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

✓ Epoxy vitrimers	Imine	Dyn Cov Bond
Prep	▪ Curing mono-glycidyl structure of vanillin (Van-Ep) with isophorone diamine (IPDA) hardener	✓ Product vanillin-based epoxy vitrimer (Van-Ep/IPDA) with dynamic imine covalent bonds
Prop	▪ Excellent reprocessability ▪ Acid degradable behavior	

Vanillin-based degradable epoxy vitrimers: Reprocessability and mechanical properties study	European Polymer Journal, 117(2019)55-63 doi.org/10.1016/j.eurpolymj.2019.04.053
Qingqing Yu and Xionghou Peng and Yuli Wang and Hongwei Geng and Anchang Xu and Xi Zhang and Weilin Xu and Dezhan Ye	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Vitrimers: Associative dynamic covalent adaptive networks in thermoset polymers	Chemical Engineering Journal, 385(2020)123820 doi.org/10.1016/j.cej.2019.123820
Balaji Krishnakumar and R.V.S. Prasanna Sanka and Wolfgang H. Binder and Vijay Parthasarthy and Sravendra Rana and Niranjan Karak	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Epoxy resins

Epoxy resin		Dyn. Cov. Bonds
Recycling	hot pressing	
Prep	Vanillin + polyimine-epoxy cross-linked network → in-situ formation of the schiff base st	
o Chemical structures o Thermal and mechanical properties	o Fourier transform infrared spectroscopy o Nuclear magnetic resonance spectra o Differential scanning calorimetry o Dynamic thermomechanical analysis	
o Vanillin-based epoxy resin (dade) o Diglycidyl ether of bisphenol a epoxy resin (dgeba)		

A recyclable vanillin-based epoxy resin with high-performance that can compete with DGEBA	European Polymer Journal, 140(2020)110053doi.org/10.1016/j.eurpolymj.2020.110053
Xunzheng Su and Zhen Zhou and Jingcheng Liu and Jing Luo and Ren Liu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

▪ Healable polymer ▪ Shape memory polymer	+ Thermosets + Enable recycling	Dynamic Covalent Bond
Prep	Esterification of diglycidyl ether of bisphenol A + tricarballylic acid.	
healing efficiency	~60%	

Intrinsic healable and recyclable thermoset epoxy based on shape memory effect and transesterification reaction	Polymer, 105(2016)10-18 doi.org/10.1016/j.polymer.2016.10.013
Lu Lu and Jizhou Fan and Guoqiang Li	

Malleable and Recyclable Thermosets:The Next Generation of Plastics	Matter 1(2019)1456–1493
Yinghua Jin, Zepeng Lei, Philip Taynton, Shaofeng Huang, and Wei Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Thermosets

Plastics	o	Dyn Cov Chem
Malleable thermosets:	☞ crosslinked polymers with dynamic covalent bonds, ☞ Bonds cleaved and reformed reversibly	
	Excellent mechanical properties and thermal and chemical stabilities like traditional thermosets + Reprocessable recyclable like thermoplastics	
Highlights Rev*	☞ Introduction of fundamental concepts ☞ Dynamic covalent chemistry -- covalent adaptable network--malleable thermosets, -- rehealability, possible recyclability--recent literature examples ☞ Future opportunities	

Malleable and Recyclable Thermosets: The Next Generation of Plastics	Matter, 1 (2019) 1456-1493 doi.org/10.1016/j.matt.2019.09.004
Yinghua Jin and Zepeng Lei and Philip Taynton and Shaofeng Huang and Wei Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Ultrastrong intrinsic bonding for thermoset composites via bond exchange reactions	Composites Part B: Engineering, 194(2020)108054 doi.org/10.1016/j.compositesb.2020.108054
Zhiqiang Chen and Qian Shi and Xiao Kuang and H. Jerry Qi and Tiejun Wang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

covalent organic frameworks

Covalent organic framework	Rev	Dyn. Cov.Chem
Highlights Rev*	☞ Porphyrin ☞ Phthalocyanine	☞ Catalysis ☞ Optoelectronic devices

Dynamic Combinatorial Evolution within Self-Replicating Supramolecular Assemblies	Angew. Chem. Int. Ed.48(2009)1093-1096 DOI: 10.1002/anie.200804602
Remi Nguyen, Lionel Allouche, Eric Buhler and Nicolas Giuseppone	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Dynamic combinatorial chemistry	Rev	Dyn. Cov.Bond
KeyLrn_Bits	☞ Folding or self-replicating macrocycles ☞ Emergence of life from a pool of simple chemicals ☞ Kinetic and thermodynamic control coexist in DCC ☞ Non-covalent interactions	

Evolution of Dynamic Combinatorial Chemistry	Acc Chem Res.,45(2012) 2211-21 doi: 10.1021/ar200240m
Fabien B. L. Cougnon And Jeremy K. M. Sanders	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_In

Rev	covalent organic frameworks	Dyn. Cov.Chem
KeyLrn_Bits	☞ modulation, mixed linker ☞ linker exchange	☞ substoichiometric reaction ☞ isomerism

Applications of Dynamic Covalent Chemistry Concept toward Tailored Covalent Organic Framework Nanomaterials: A Review	ACS Appl. Nano Mater.(2021) doi.org/10.1021/acsanm.0c01327
Jiyun Hu, Suraj K. Gupta, John Ozdemir, and M. Hassan Beyzavi	

Covalent organic frameworks (Cov Org FraWrk)		Dyn Cov Bonds
Highlights of rev	🕮 Synthetic strategies with special emphasis on dynamic covalent chemistry 🕮 Strategies of introducing extra tools in COFs to enhance their crystallininty, porosity and chemical stability	
Applications of COFs	🕮 CO_2 capture 🕮 Important parameters in the applications of COFs for post-combustion capture of CO_2 in the CCS technology	

Recent advances in the synthesis of covalent organic frameworks for CO2 capture	Journal of CO2 Utilization, 17(2017)137-161 doi.org/10.1016/j.jcou.2016.12.003
Abass A. Olajire	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

☞ Porous polymers	☞ Cov org frameworks	Dyn Cov Chem
Synth:	Dehydration of a tetrahedral tetrakis(boronic acid) monomer → boroxine-linked 3D network	
Prop of COF-102 network	high functionalization density, long-range order, and permanent porosity.	

Functionalization of 3D covalent organic frameworks using monofunctional boronic acids	Polymer, 55(2014)330-334 doi.org/10.1016/j.polymer.2013.07.030
Spencer D. Brucks and David N. Bunck and William R. Dichtel	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

✓ Imines	Self-assembly	Dyn Cov Chem Cov Org frameworks
Factors affecting yield	✓ Reaction solvent ✓ Composition ✓ Structure of building units influence	✓ Reaction kinetics and thermodynamics ✓ Degree of condensation

Thermodynamic, kinetic, and structural factors in the synthesis of imine-linked dynamic covalent frameworks	Tetrahedron, 68(2012)53-64 doi.org/10.1016/j.tet.2011.10.052
Nathan C. Duncan and Benjamin P. Hay and Edward W. Hagaman and Radu Custelcean	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Review		Dyn Cov Chem Covalent Organic Frameworks
KeyLrn_Bits	Post-synthetic modification	+ Stability + linkage,
Covalent organic frameworks (COFs)	These are functional porous crystalline "molecular Legos" Composed of light elements Held together by covalent bonds.	
Synthesis	Relies on the formation of reversible covalent bonds linking multivalent monomers	
Reversibility	Imparts error correction & defect healing	
Highlights of Rev	State-of-the-art development of chemically robust cofs, Scrutinize the intriguing	
Applications	Heterogeneous catalysis Environmental remediation Chiral separation, Corrosive gas sensing, and Lithium-ion batterie	
Future research	Major challenges Opportunities in future research directions \ Perspectives of chemically robust co`fs.}	

Chemically Robust Covalent Organic Frameworks: Progress and Perspective	Matter, 3(2020)1507-1540 doi.org/10.1016/j.matt.2020.09.007
Xinle Li and Songliang Cai and Bing Sun and Chongqing Yang and Jian Zhang and Yi Liu	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

metal-organic frameworks		Dyn Cov Chem
KeyLrn_Bits	▪ Combination of dynamic covalent chemistry + coordination chemistry in MOFs ▪ Post-synthetic methods, ▪ Interpenetration	▪ Benchmark ▪ Expansion contraction ▪ Flexibility, ▪ Stability and lability

Lattice Expansion and Contraction in Metal-Organic Frameworks by Sequential Linker Reinstallation	Matter, 1(2019)156-167 doi.org/10.1016/j.matt.2019.02.002
Liang Feng and Shuai Yuan and Jun-Sheng Qin and Ying Wang and Angelo Kirchon and Di Qiu and Lin Cheng and Sherzod T. Madrahimov and Hong-Cai Zhou	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Compd	Cucurbiturils (CB)	Dyn Comb Lib Dyn Comb Bonds
Overview of CB formation mechanisms Synthetic methods	Prop	✓ Dimensions shapes of cucurbituril derivatives ✓ Solubilities in water

3.08 - Cucurbiturils: Synthesis, Structures, Formation Mechanisms, and Nomenclature	Comprehensive Supramolecular Chemistry II, Elsevier (2017)203-220 doi.org/10.1016/B978-0-12-409547-2.12514-4
R. Aav and S. Kaabel and M. Fomitšenko	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Diselenide bonds

Dynamic diselenide bonds	! Network polymers	Dyn. Cov. Bonds
	! Polymer reactions\ Diselenide, ! Network polymers	

If	there are neighboring aromatic rings instead of aliphatic derivatives
Then	Dynamic properties (ex. Higher photo-stability against UV light) enhanced for diselenide bonds

Enhancement of the stimuli-responsiveness and photo-stability of dynamic diselenide bonds and diselenide-containing polymers by neighboring aromatic groups	Polymer,154(2018)281-290 doi.org/10.1016/j.polymer.2018.09.022
Nao Suzuki and Akira Takahashi and Tomoyuki Ohishi and Raita Goseki and Hideyuki Otsuka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Disulfide	Dyn Cov Chem Dyn Comb Chem	
KeyLrn_Bits	▪ RNA ▪ Peptides	▪ HIV

Probing the geometric constraints of RNA binding via dynamic covalent chemistry	Bioorganic & Medicinal Chemistry, 24(2016)3940-3946 doi.org/10.1016/j.bmc.2016.02.029
John D. McAnany and John P. Reichert and Benjamin L. Miller	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Miscellaneous

		Dynamic Covalent Chem
KeyLrn_Bits	▪ Rhombimines ▪ Chiral diacetals ▪ Schiff-base macrocycles	▪ Spiro atom ▪ TDDFT calculations

Axial chirality inversion at a spiro carbon leads to efficient synthesis of polyimine macrocycle	Journal of Molecular Structure, 1202(2020) doi.org/10.1016/j.molstruc.2019.127336
Mikołaj Zgorzelak and Jakub Grajewski	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Compd	Triphenylamines	Dyn Comb Lib Dyn Comb Bonds
🕮 Reversible Diels-Alder reaction of these dyes → ➔ Reversible emission switch OFF/ON		

Dynamic dye emission ON/OFF systems by a furan moiety exchangeprotocol	Dyes and Pigments, 184(2021)108652 doi.org/10.1016/j.dyepig.2020.108652
Qi Zhang and Ying Wang and Junbo Gong and Xin Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Compd	☞ Benzo[ghi]perylene trimide, ☞ Perylene diimide,	Dyn Comb Chem
Synth	▪ Benzo[ghi]perylene trimide ▪ its anion radical π-bonded dimer	

Structural, photoelectrical and thermol properties of ultra-stable Benzo[ghi]perylene trimide dimer anion	Tetrahedron,75 (2019) 130577 doi.org/10.1016/j.tet.2019.130577
Siyu Wu and Caihong Cheng and Wenlong Hou and Qizhe Li and Danyang Dong and Yongshun Gao and Lu Liu and Bo Liang and Haiquan Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Compd	☞ Polybutadiene or ☞ Naturally occurring o Polyisoprene o Olefin-containing polyurethane	Dyn Cov Chem	
Factors studied :	! Reaction time ! Solvent ! Homopolymer structure	Prop:	Enhanced mechanical properties

Metathesis-driven scrambling reactions between polybutadiene or naturally occurring polyisoprene and olefin-containing polyurethane	Polymer, 78(2015)145-153 doi.org/10.1016/j.polymer.2015.09.076
Tomoyuki Ohishi and Kaori Suyama and Shigehisa Kamimura and Masahide Sakada and Keiichi Imato and Seiichi Kawahara and Atsushi Takahara and Hideyuki Otsuka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Aromatic compounds	o Self-assembly o Molecular recognition	Dyn Cov Chem	
Compd	10-Hydroxy-10,9-boroxophenanthrene + benzylic and alkane diols → 2:1 adducts	Reversible covalent chemistry	

The dynamic covalent chemistry of mono- and bifunctional boroxoaromatics	Tetrahedron, 63(2007) 2391-2403 doi.org/10.1016/j.tet.2006.12.034
Lyndsey M. Greig and Alexandra M.Z. Slawin and Melanja H. Smith and Douglas Philp	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

▪ Phenylboronic acid		Dynamic Covalent Chem
KeyLrn_Bits	▪ Electrochemical biosensor, ▪ Cells capture and release, ▪	▪ Tumor cells, Diagnosis
Electrochemical biosensor ▪ Promising platform ▪ Specific tumor cell detection ▪ Monitoring the cell capture and release		Future diagnosis ▪ Early discovery detection of o Tumorigenesis o Metastasis

A dynamic electrochemical cell sensor for selective capture, rapid detection and noninvasive release of tumor cells	Sensors and Actuators B: Chemical, 330(2021)129345 doi.org/10.1016/j.snb.2020.129345
Xiaohua Tian and Yonghai Feng and Liang Yuan and Yuqing Duan and Lei Liu and Mingdong Dong	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

	✓ Atom transfer radical polymerization ✓ Block copolymers	Dyn.Comb.Chem
Synth	Atom transfer radical polymerization of monomers using a bis-bromoisobutyrate initiator bearing one acylhydrazone bond → Dynamic polystyrene (d-PS) and poly(n-butyl acrylate) (d-PBA) with an acylhydrazone linkage at each chain center	

If	treated with trifluoroacetic acid or heated at 120 °C in solution
Then	polymer chains of d-PS and d-PBA were found to be cleaved

	partially into blocks of half original length → implies a dynamic equilibrium of forming and breaking acylhydrazone bond	

Dynamic polymers containing one acylhydrazone linkage and dynamic behavior thereof	Polymer, 54(2013)2647-2651 doi.org/10.1016/j.polymer.2013.03.023
Zizhen Xu and Peng Zhao and Yongming Chen and Guohua Deng	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Diels-Alder reaction Cyclic polymer	Epoxy resins	Dyn Cov Bond
Prep	Cyclic poly(methyl methacrylate) linked by a dynamic covalent furan/maleimide bond was rationally designed	

Degradable epoxy resins prepared from diepoxide monomer with dynamic covalent disulfide linkage	Polymer, 82(2016)319-326 doi.org/10.1016/j.polymer.2015.11.057
Akira Takahashi and Tomoyuki Ohishi and Raita Goseki and Hideyuki Otsuka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Perylene bisimide derivatives	☞ Fluorescence sensing, ☞ To develop functionality-led molecular systems	Dyn Cov Chem
Preparation	Fluorescent ionic complex : 3,4,9,10-perylene tetracarboxylic acid (PTCA)	Acid-base reaction with (2-(6-aminohexanamido)phenyl)boronic acid (PBA- NH2)
Effect on Response fluorescence	If Fluoride introduced, it turns the quenched fluorescence on	
	If Ca2+ added, it makes emission off again	
	Reason: Formation and disruption of dynamic cyclic boronate esters owing to establishment and cleavage of another dynamic covalent bond of B-F ➔ Accordingly, selective and reversible sensing of glucose (PVA), F− and Ca2+ was realized	

Formation of an ionic PTCA-PBA-NH2 complex and its fluorescent changes triggered by cyclic boronate ester establishing and cleavage reaction	Journal of Photochemistry and Photobiology A: Chemistry, 355(2018)425-40 doi.org/10.1016/j.jphotochem.2017.07.020
Xiaojie Xu and Huijing Liu and Qingqing Sun and Xuwei Fu and Rongrong Huang and Yu Fang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

☞ Trianglamines ☞ Calixsalan ☞ Imine	☞ Isotrianglamine, Macrocycle ☞ Rhombamine, Supramolecular	Dyn Cov Chem
Synth:	Primary amines + Aldehydes →	Macrocyclic imines under thermodynamic equilibrium conditions

Prop	☞ Macrocyclic imines are rigid, ☞ Imine reduction products, oligoamines are flexible
Appl	☞ Chiral discrimination in NMR spectroscopy ☞ For asymmetrical catalysis
Basis of	Imine synth is Dyn cov bond formation between primary amines and aldehydes

3.11 - Trianglamines and Related Chiral Macrocycles	Comprehensive Supramolecular Chemistry II, Elsevier(2017)267-291 doi.org/10.1016/B978-0-12-409547-2.12521-1
J. Gawroński and M. Kwit and U. Rychlewska	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

▪ Thermo-mechanical response		+ Dynamic Covalent Bond
KeyLrn_Bits	+ Constitutive modeling , +	+ Elastomer + Nanocomposite

Natural and synthetic rubbers : Networks of polymer chains connected by irreversible chemical cross-links

- Cannot be repaired after damage
- Discarded rubbers cannot be economically recycled and reprocessed

Elastomers with dynamic covalent bonds

+ Recyclability, Malleability; Capability of Autonomous Self-Healing

Expl: Thermally triggered bond-exchange reactions

Structure–property relations over wide range of temperatures

Material parameters	Materials
✓ Tensile tests ✓ Cyclic tests ✓ Relaxation tests ✓ creep tests	✓ Covalently cross-linked rubber, ✓ Thermoplastic elastomer ✓ Elastomer anocomposites with dynamic covalent bonds ✓ epoxy vitrimers

Thermo-mechanical behavior of elastomers with dynamic covalent bonds	International Journal of Engineering Science, 147(2020) 103200 doi.org/10.1016/j.ijengsci.2019.103200
A.D. Drozdov and Jesper deClaville Christiansen	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Polymer reactions		Dyn Cov Chem

KeyLrn_Bits	▪ Cross-linked polymers, ▪ Polymer/silica composites	▪ EPR spectroscopy
☞ Exchangeable dynamic covalent carbon–carbon bonds introduced into of polymer/silica composites→	Structural reorganization	

Network reorganization in cross-linked polymer/silica composites based on exchangeable dynamic covalent carbon–carbon bonds	Polymer, 177(2019)10-18 doi.org/10.1016/j.polymer.2019.05.046
Takahiro Kosuge and Daisuke Aoki and Hideyuki Otsuka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

☞ Macrocycles		Dyn Cov Chem
Synth of	☞ Stereoselective synthesis of first representatives of 1,12-diaza-3,10,14,21-tetra-phospha-cyclo-docosanes	By Mannich-type condensation : 1,6-bis(phenylphosphino)hexane + formaldehyde + primary amines

Stereoselective synthesis of the RPSPSPRP isomer of 22-membered P4N2 macrocycles	Mendeleev Communications, 30(2020) 697-699 doi.org/10.1016/j.mencom.2020.11.002
Elvira I. Musina and Tatiana I. Wittmann and Alena S. Shpagina and Andrey A. Karasik and Peter Lönnecke and Evamarie Hey-Hawkins	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dyn Cov Chem
Nucleic acids	➔ Central role in storing and transmitting genetic information ➔ High-specificity, high-affinity hybridization 📖 Appl: Gene therapy, agricultural disease management, electronics	
KeyLrn_Bits	▪ Xenonucleic acid ▪ Click chemistry ▪ Template-directed synthesis	▪ Nucleic acid ▪ Xenonucleic acids (XNAs)
XNA synthesis	Influenced by ☞ Biology (e.g., directed evolution) ☞ Chemistry (e.g., dynamic covalent reactions)	

Towards High-Efficiency Synthesis of Xenonucleic Acids	Trends in Chemistry,2(2020)43-56 doi.org/10.1016/j.trechm.2019.06.004
Benjamin D. Fairbanks and Heidi R. Culver and Sudheendran Mavila and Christopher N. Bowman	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Controlled-release system Next generation		Dyn Cov Chem
KeyLrn_Bits	▪ -hexylimine-chitosan ▪ Hexanal	▪ Antifungal ▪ Grain storage ▪ Biodegradable
Prep of	☞ Iminated N-hexylimine-chitosan (NHIC)by	☞ Reaction of Polysaccharide chitosan + hexyl aldehyde in Schiff base
Appl	☞ Decrease in the mold occurrence on the grain	

N-hexylimine-chitosan, a biodegradable and covalently stabilized source of volatile, antimicrobial hexanal. Next generation controlled-release system	Food Hydrocolloids, 48(2015)213-219 doi.org/10.1016/j.foodhyd.2015.02.033
Tania Fadida and Adi Selilat-Weiss and Elena Poverenov	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Controlled-release system Next generation		Dyn Cov Bond
Synth of	☞ Assembling multi-hydroxyl carbon dots (CDs) on magnetic nanoparticles ☞ Modified with phenylboronic acid (PBA) molecular brush by a reversible dynamic covalent bond	
Appl	☞ Glucose monitoring	+ High sensitivity + Wide linear response range from 0.2 to 20 mM of glucose

Glucose assay based on a fluorescent multi-hydroxyl carbon dots reversible assembly with phenylboronic acid brush grafted magnetic nanoparticles	Sensors and Actuators B: Chemical, 304(2020)127349 doi.org/10.1016/j.snb.2019.127349
Ji Li and Xinjie Li and Rongqin Weng and Taotao Qiang and Xuechuan Wang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

		Dyn Cov Chem
Synth of	☞ Polybutadienes and olefin-containing polyurethanes + With urethane linkages as a source of hydrogen bonds in the polymer main chain (PBUs).	
Appl	▪ Cured rubbers + Durability and fuel efficiency	
KeyLrn_Bits	☞ Rubber ☞ Toughness	+ Hydrogen bonds + Energy dissipation,

Polybutadiene rubbers with urethane linkages prepared by a dynamic covalent approach for tire applications	Polymer, 202(2020)122700 doi.org/10.1016/j.polymer.2020.122700
Yasuhiro Shoda and Daisuke Aoki and Katsuhiko Tsunoda and Hideyuki Otsuka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Imines		Dyn Cov Chem
KeyLrn_Bits	▪ Cages ▪ Self-assembly	▪ Supramolecular chemistry

Dyn Cov Chem	Viable approach for the preparation of complex organic compounds
Synth of tris-imine	🕮 C3-symmetric trialdehyde + triamine in acetonitrile 🕮 Catalyst : trifluoroacetic acid + Dynamic Covalent Bond Formation

Synthesis of a C3-symmetric tris-imine via dynamic covalent bond formation between a trialdehyde and a triamine	Tetrahedron Letters, 58(2017)4612-4616 doi.org/10.1016/j.tetlet.2017.10.061
Keiko Nakada and Seiya Kondo and Yoshiteru Matsumoto and Masamichi Yamanaka	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

DCB-69		
		Dyn Cov Bond
KeyLrn_Bits	▪ Self-assembly	▪ Carbohydrate
Supra-amphiphile	☞ Azobenzene-galactopyranoside (Azo-Gal) supra-amphiphile ☞ Self-assembled to fibrillar structure in water	
Dual responses to	🕮 UV light and pH	

Self-assembly of supra-amphiphile of azobenzene-galactopyranoside based on dynamic covalent bond and its dual responses	Chinese Chemical Letters, 27(2016)1740-1744 doi.org/10.1016/j.cclet.2016.05.009
Tian-Nan Wang and Guang Yang and Li-Bin Wu and Guo-Song Chen	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Aromatic disulfides Polysiloxanes	Outstanding reprocessability	Dyn Cov Bond
ATP3-SS showed best stretchability	Elongation at break was as high as 780%.	
APP1-SS achieved highest tensile strength of	2.60 MPa	

Stretchable, robust and reprocessable poly(siloxane-urethanes) elastomers based on exchangeable aromatic disulfides	Polymer, 221(2021)123588 doi.org/10.1016/j.polymer.2021.123588
Shijie Shan and Yaling Lin and Anqiang Zhang	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Chitosan Self-healing	Chitosan hydrogels using monoaldehydes + Widespread in nature + Cheap + Beneficial to the human body	Dyn Cov Chem,
KeyLrn_Bits	▪ Superporous ▪ Luminescence	▪ Thixotropy ▪ bio-medical applications

Salicyl-imine-chitosan hydrogels: Supramolecular architecturing as a crosslinking method toward multifunctional hydrogels	Carbohydrate Polymers, 165(2017)39-50 doi.org/10.1016/j.carbpol.2017.02.027
Manuela-Maria Iftime and Simona Morariu and Luminita Marin	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Self-assembly		Dyn Cov Bond Coordination bond,
KeyLrn_Bits	▪ Supramolecular Chemosensor arrays ▪ Pattern recognition	▪ Inter/intramolecular interaction
Rev Highlights		
Conventional design strategy	▪ For chemosensor arrays -- overview of simple minimized -- multifunctional chemosensor arrays -- multi-analyte detection	
Self-assembled chemo-sensor arrays	▪ Information-rich patterns from a smaller number of chemosensors ▪ Appl: environmental and biochemical tasks ▪ Inter- or intramolecular interactions	
Self-assembly "without" a chemo-sensor array	▪ For pattern recognition ex: chirality sensing	
Knowledge-toDate	▪ To develop "sophisticated chemosensor arrays" applicable for real-world scenarios	

Molecular self-assembled chemosensors and their arrays	Coordination Chemistry Reviews, 429(2021)213607 doi.org/10.1016/j.ccr.2020.213607
Yui Sasaki and Riku Kubota and Tsuyoshi Minami	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Phosphonium salt having a dynamic covalent bond	☞ Dyn Cov Bond ☞ Between anion and cation ☞ → Enabling reversible structural shift between free ion pair and zwitterion	Dyn Cov Bond
KeyLrn_Bits	▪ Ionic liquid ▪ Phase separation	▪ Zwitterion,
Phosphonium salt macroscopic phase behavior in aqueous solution	▪ i.e. Forming Mono- Or Bi-Phasic Systems ▪ →Leading to green separation systems	
INFLUENcing factors	▪ CO_2/N_2 bubbling or ▪ Acid/base	

Hand-holding and releasing between the anion and cation to change their macroscopic behavior in water	Green Energy & Environment, 4(2019)127-130 doi.org/10.1016/j.gee.2018.12.004
Kosuke Kuroda and Yumiko Shimada and Kenji Takahashi	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Rotaxanes,	☞ Organic frameworks	Dyn Cov Chem

Macrocycles		
KeyLrn_Bits	▪ , Hydrogen bonding ,	▪ Thermodynamic control
Prep	Coupling reaction ▪ Bromopyrido-24-crown-8 + phenylboronic acid → ▪ 4-phenylpyrido-24-crown-8 (prod) ▪ Prod complexes with a variety of dibenzylammonium ions →complexes molecules ▪ Stabler than their dibenzo-24-crown-8 counterparts	
	▪ A complex in which diformyl-terminated thread is bound, → used to assemble a [2]rotaxane under thermodynamic control	

Bromopyrido-24-crown-8: a versatile building block for the construction of interlocked molecules	Tetrahedron Letters, 57(2016)513-516 doi.org/10.1016/j.tetlet.2015.11.105
Luke C. Delmas and Nicholas A. Payne and Avril R. Williams	

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Dynamic combinatorial Libraries

		Dyn. Cov.Chem
Highlights Rev*	☞ Dynamic combinatorial Libraries ☞ Dynamic combinatorial molecular networks ☞ Systems chemistry ☞ DCLs that are under thermodynamic control → o Synthetic receptors o Catalytic systems o Complex self assembled supramolecular architectures ☞ Principles of DCC to systems that are not at equilibrium ☞ → Harbor richer functional behavior o Self-replication o Molecular machines.	

Dynamic Combinatorial Libraries: From Exploring Molecular Recognition to Systems Chemistry	J. Am. Chem. Soc. 135(2013) 9222−9239dx.doi.org/10.1021/ja402586c
Jianwei Li, Piotr Nowak, and Sijbren Otto	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Double-level ‘‘orthogonal’’ dynamic combinatorial libraries on transition metal template	PNAS, 98(2001)1347–1352
Vasiliy Goral, Marina I. Nelen, Alexey V. Eliseev and Jean-Marie Lehn	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int

Selection and Amplification of Hosts From Dynamic CombinatorialLibraries of Macrocyclic Disulfides	SCIENCE, 297(2002)
Sijbren Otto, Ricardo L.E.Furlan, Jeremy K.M.Sanders	

Dyn.Cov.Bonds--Dyn.Cov..Chem--.Orthogonal.Dyn.Cov.Chem--non_cov_Int