



Sveučilište u Zagrebu

STRATEGIJE U KRISTALNOM INŽENJERSTVU VIŠEKOMPONENTNIH METALOORGANSKIH KRUTINA POVEZANIH HALOGENSKIM VEZAMA

Kemijski seminar 1

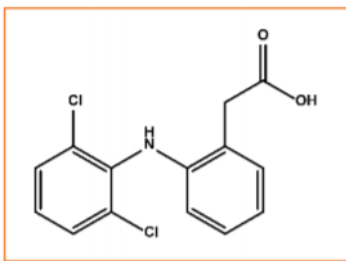
Lidija Posavec

11. svibnja 2022.

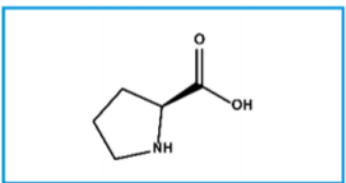
Kristalno inženjerstvo

- dizajn i priprava kristalnih materijala željenih fizikalnih i kemijskih svojstva

Diclofenac (Voltaren)

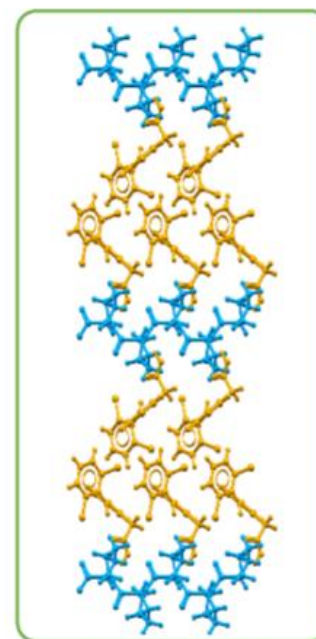


DFA



PRO

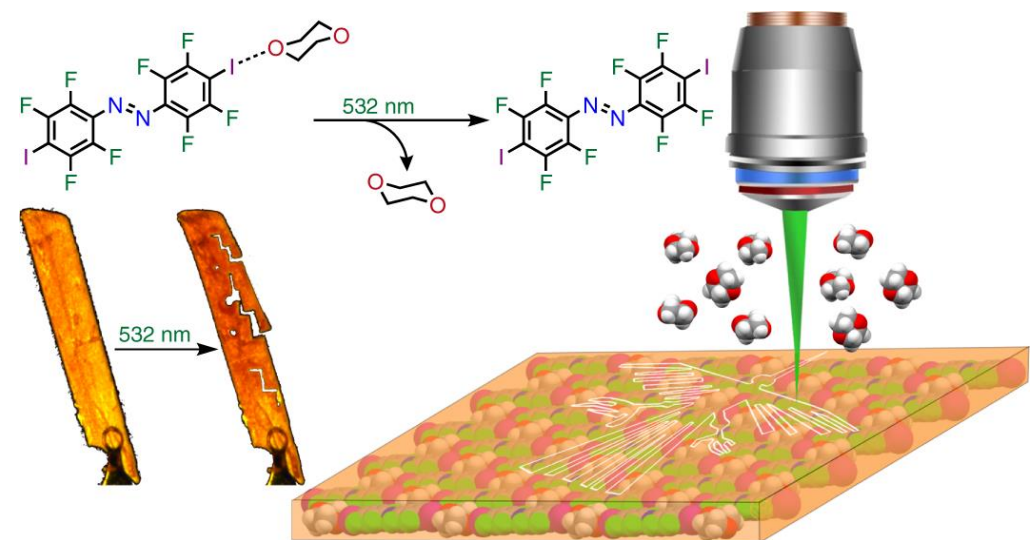
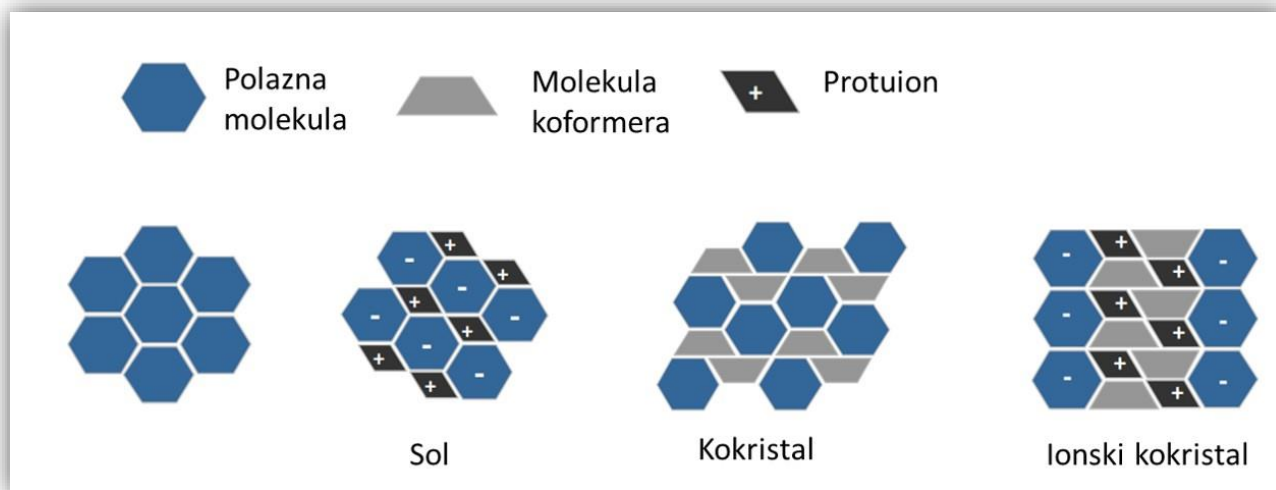
razumijevanje i primjena
neveznih interakcija



DFA-PRO

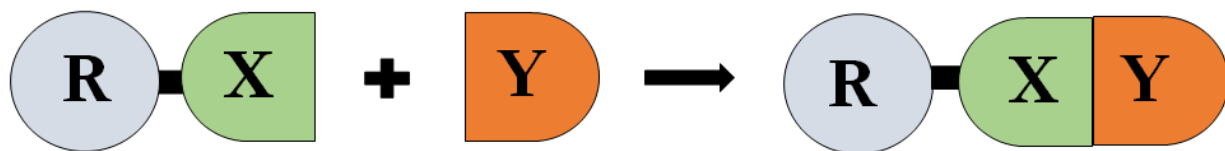
Kokristali, ionski kokristali i soli

- Kokristali - krutine sastavljene od dvije ili više različitih molekulskih komponenta u određenom stehiometrijskom odnosu, a koje sastavom ne odgovaraju solvatima ili jednostavnim solima



Halogenska veza

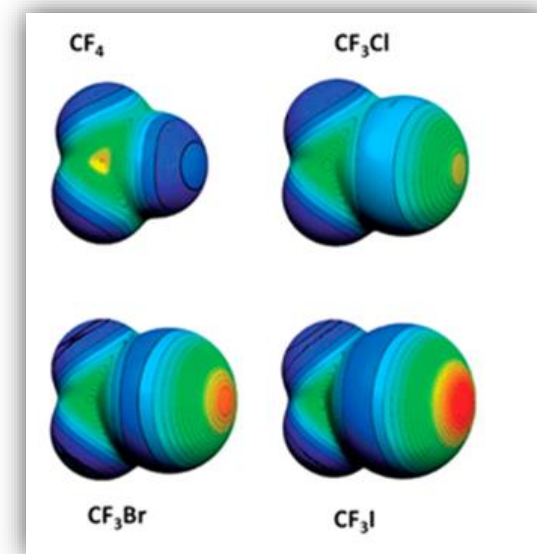
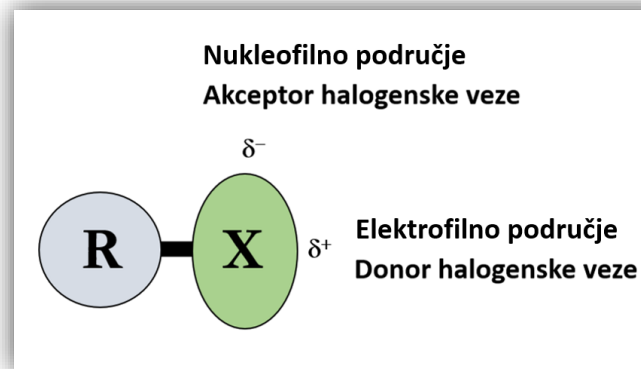
- nekovalentna interakcija koja se ostvaruje između elektrofilnog područja halogenog atoma X i nukleofilne područja atoma Y



R = C, N, F, Cl, Br, I

X = I, Br, Cl, F

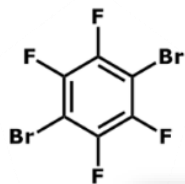
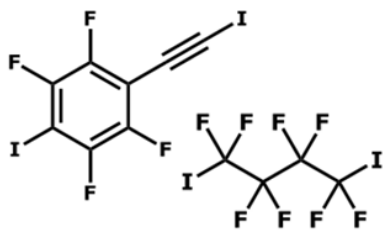
Y = N, O, S, Se, Cl, Br, I, I⁻, Br⁻, Cl⁻, F⁻



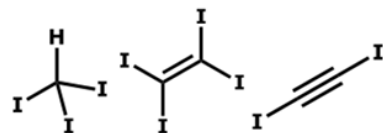
Donori i akseptori halogenske veze

DONORI

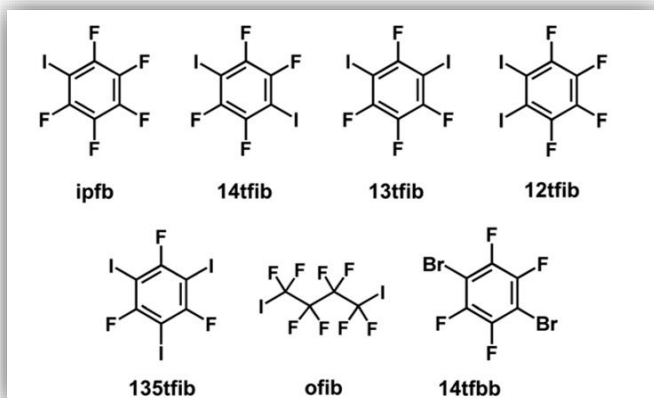
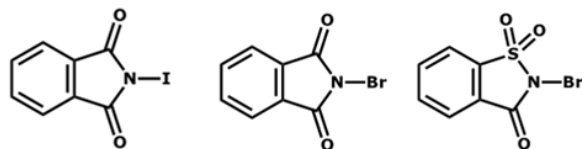
a) perhalogenirani ugljikovodici



b) halogenirani alkani, alkeni i alkini,

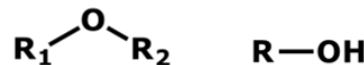


c) N-halogenimidi

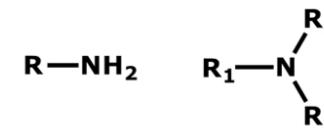
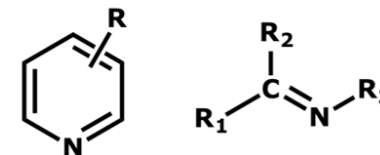


AKCEPTORI

a) atom kisika kao akceptor



b) atom dušika kao akceptor



Koordinacijski spojevi

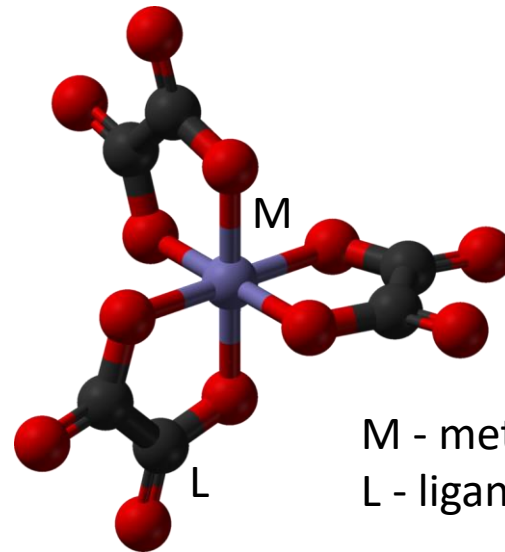
Višekomponentne metaloorganske krutine

Razlozi za korištenje koordinacijskih spojeva

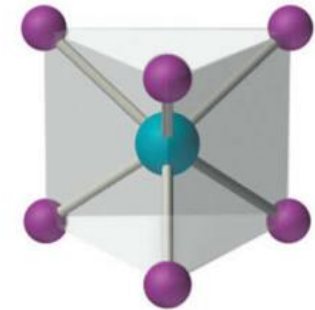
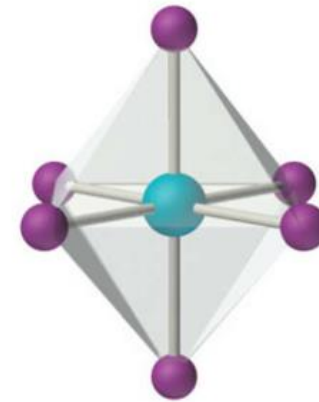
- zanimljiva magnetska, električna i optička svojstva
- mogućnost primjene u procesu katalize
- modifikacija izmjenom metalnog centra, liganada
- širok raspon različitih geometrija

Problemi:

- supstitucija liganada, izomerizacija
- otežana kontrola konačne konfiguracije
- kompeticija liganda za metalni centar



M - metalni centar
L - ligand



Višekomponentne metaloorganske krutine

- a) stabilnost metaloorganskog koordinacijskog spoja
- b) sposobnost da sudjeluje u interakcijama kao donor ili akceptor halogenske veze

STABILNOST

M

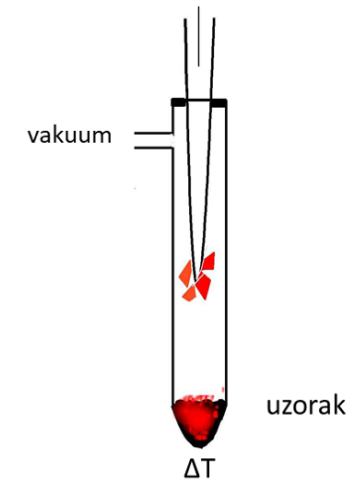
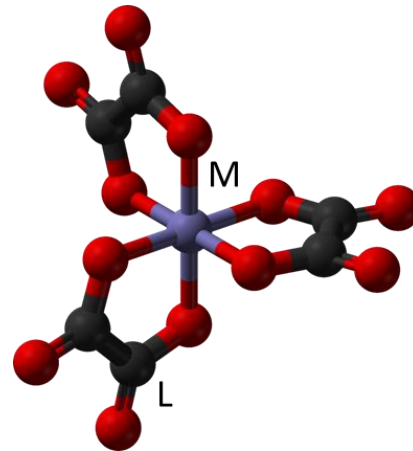
Odabir metalnog centra

L

Odabir liganda



Promjena reakcijskih uvjeta -
otapalo



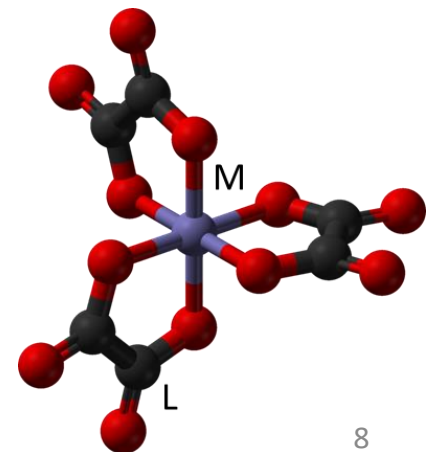
Višekomponentne metaloorganske krutine

a) odabir metalnog centra, kinetički inertni koordinacijski spojevi

(Cr^{III}, Co^{III}, Rh^{III}, Pd^{II}, Pt^{II})

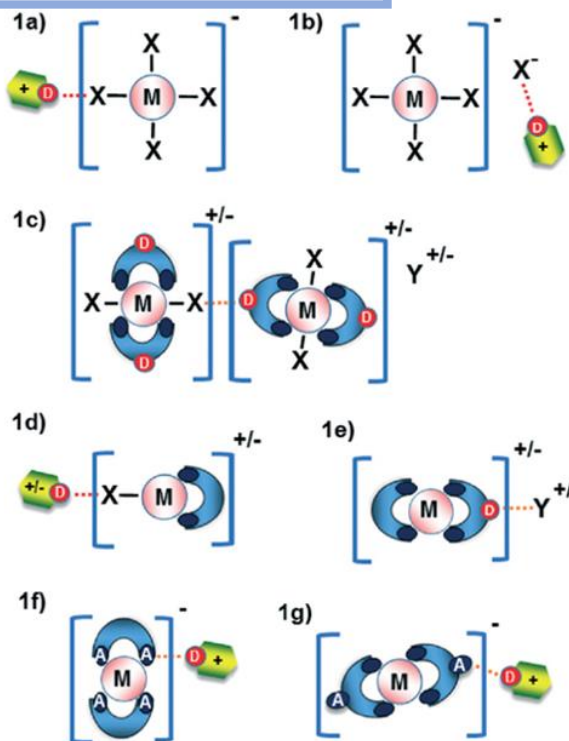
b) odabir liganda:

- inertni ligandi (Schiffove baze, β-diketoni)
- "labilni" ligandi (amini, alkoholi, ketoni, heterociklički spojevi, voda, amonijak)
- monovalnetni, anorganski anioni (halogenidi, pseudohalogenidi, oksidi, sulfidi)

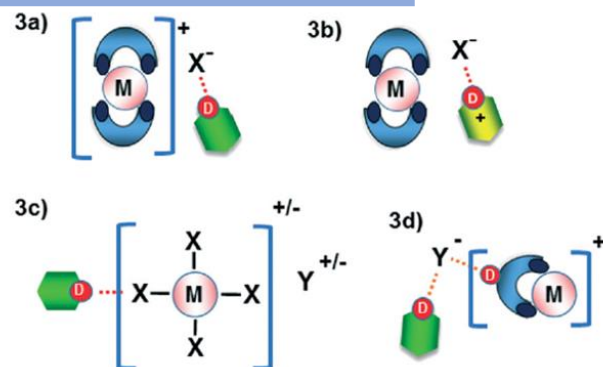


Pregled osnovnih strategija

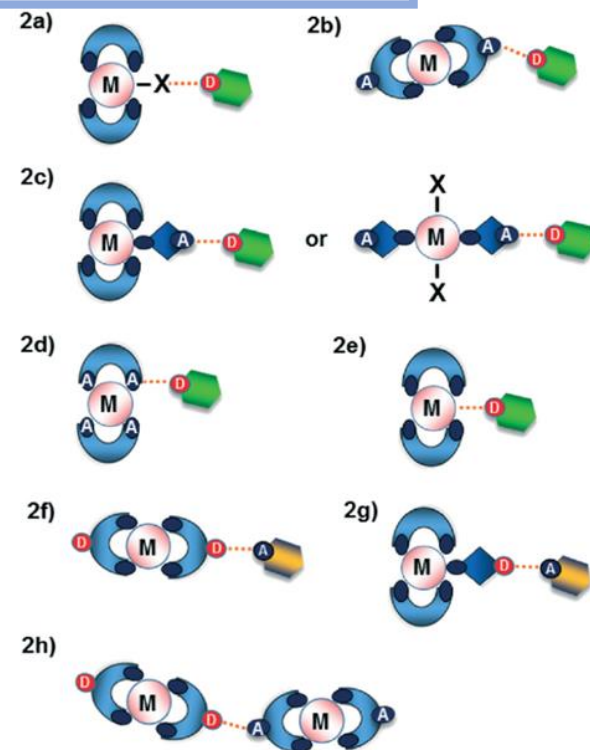
1. Metalo-organske soli



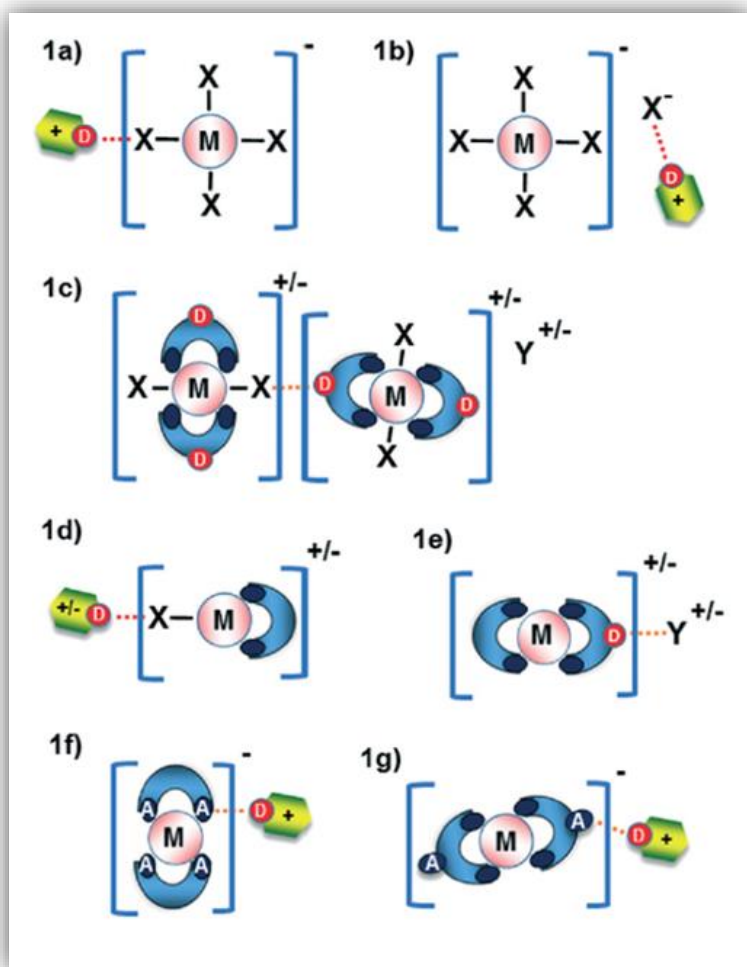
3. Metalo-organski ionski kokristali



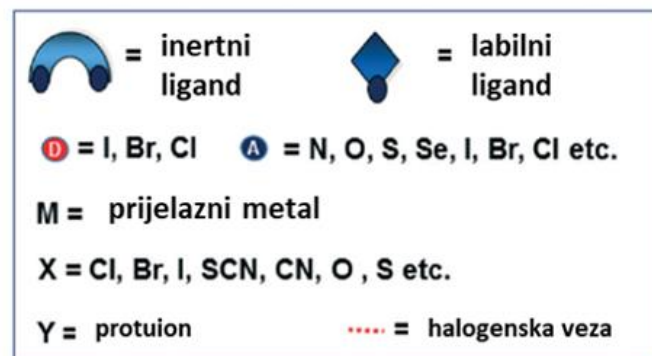
2. Metalo-organski kokristali



Metaloorganske soli

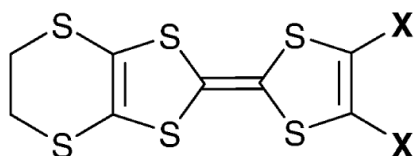


- višekomponentni sustavi u kojima su kation ili anion (ili oboje) koordinacijski spojevi, te je barem jedna komponenta donor halogenske veze
- najviše upotrebljavana je strategija **1a**, koja uključuje polihalogenometalate, pseudohalogenometalate i oksometalate kao akceptore halogenske veze



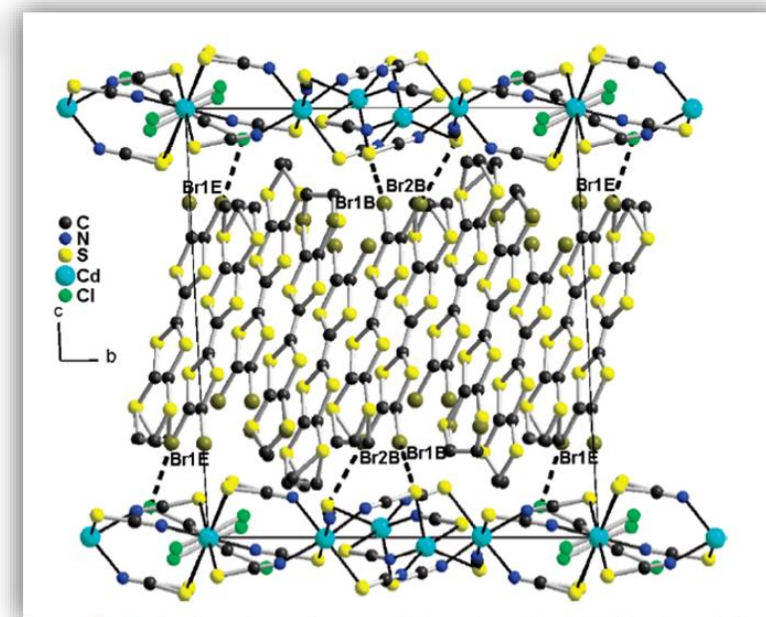
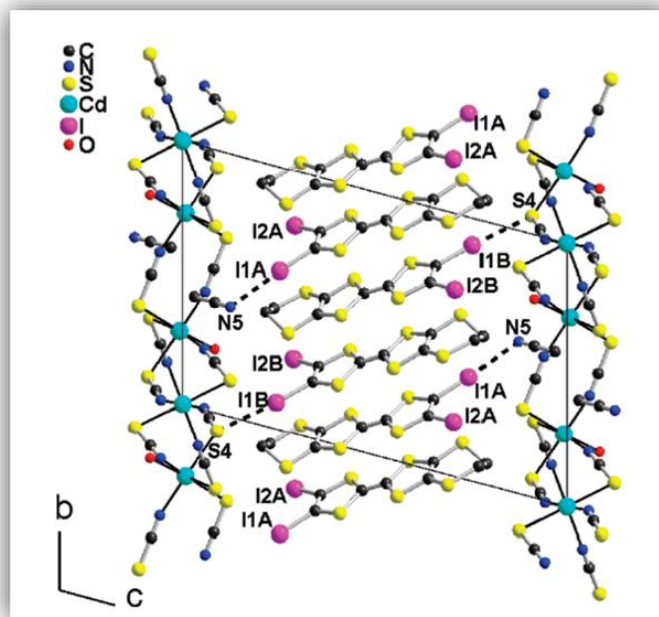
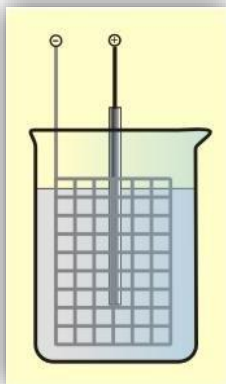
Metaloorganske soli

- molekularni vodiči koji sadrže halogenirane tetafulvalenske radikalne katione
- istraživanje električne vodljivosti soli halogeniranih tetrathiafulvalena konstruiranih pomoću polimernih lanaca $[\text{Cd}(\text{SCN})_3]_{\infty}^{-}$

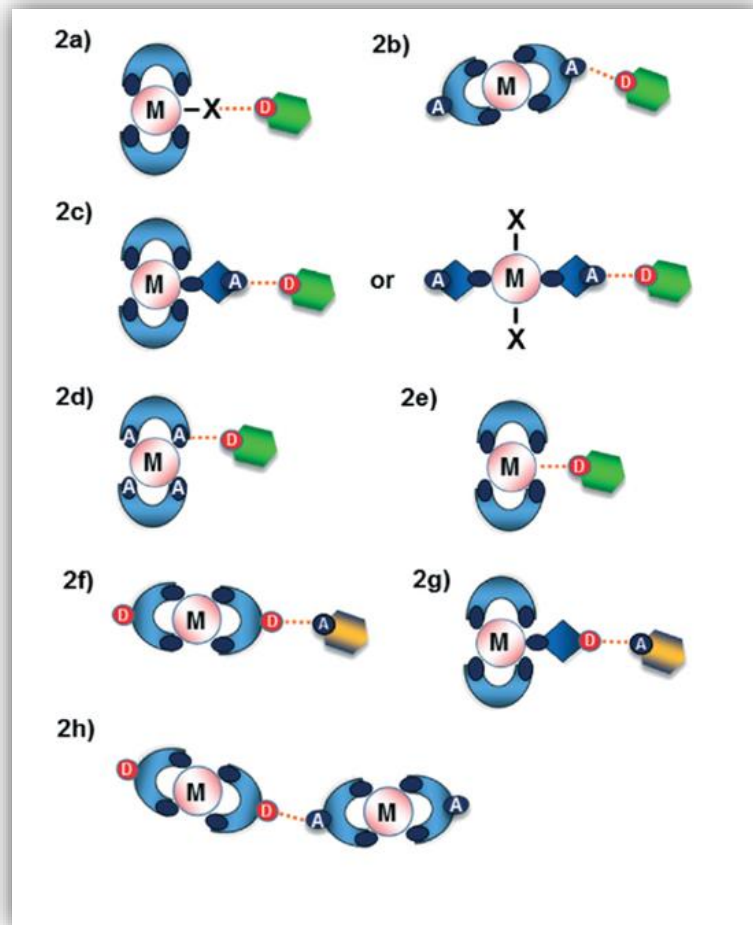


X = Br
X = I

- elektrokristalizacija

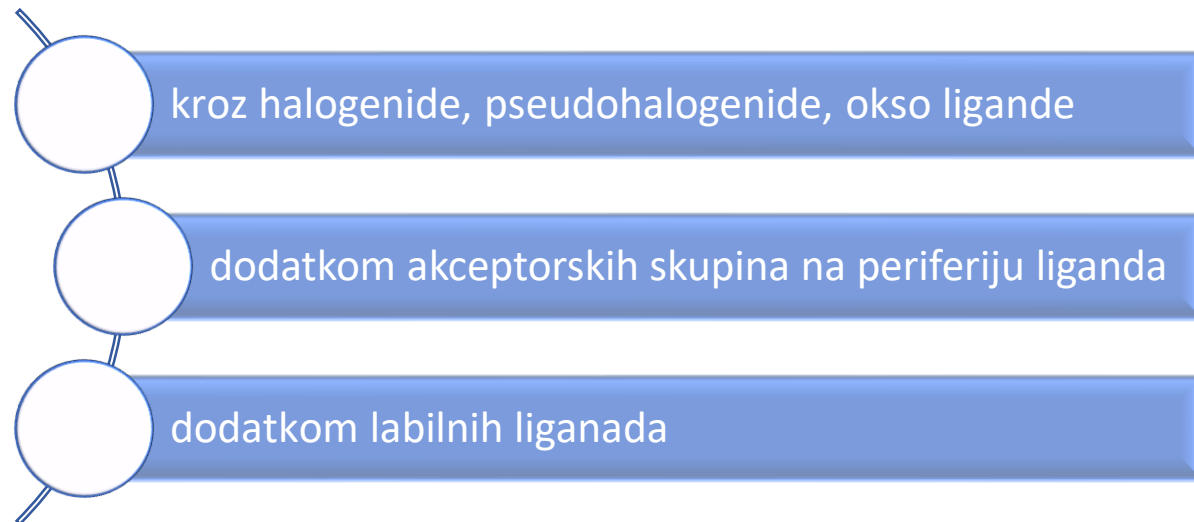


Metaloorganski kokristali

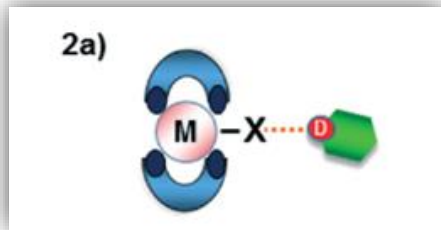


- strategije uključuju neutralne metalne komplekse kao akceptore halogenske veze i neutralne organske molekule kao donore

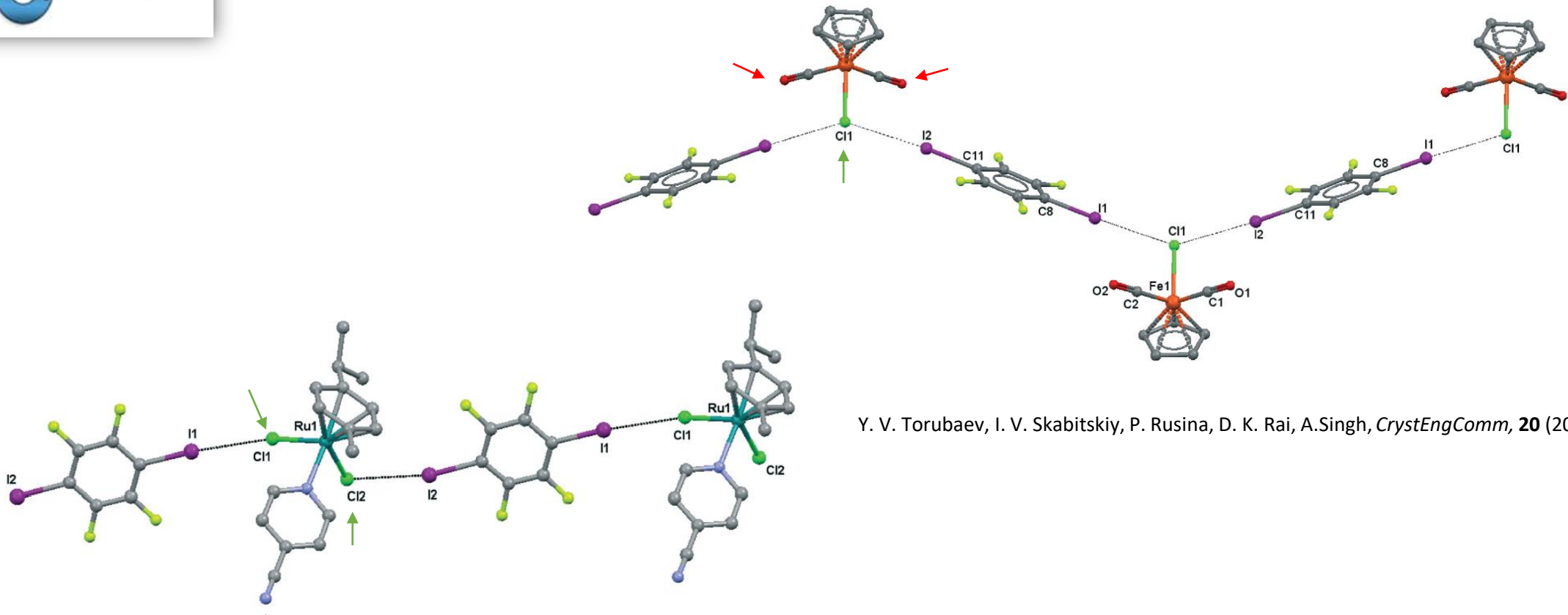
Akceptorska mjesta se na koordinacijske spojeve uvode:



Metaloorganski kokristali



- U kompeticiji s drugim akceptorskim skupinama, halogenska veza se ostvaruje prvenstveno s halogenidima.

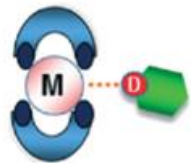


Y. V. Torubaev, I. V. Skabitskiy, P. Rusina, D. K. Rai, A. Singh, *CrystEngComm*, **20** (2018) 2258–2266.

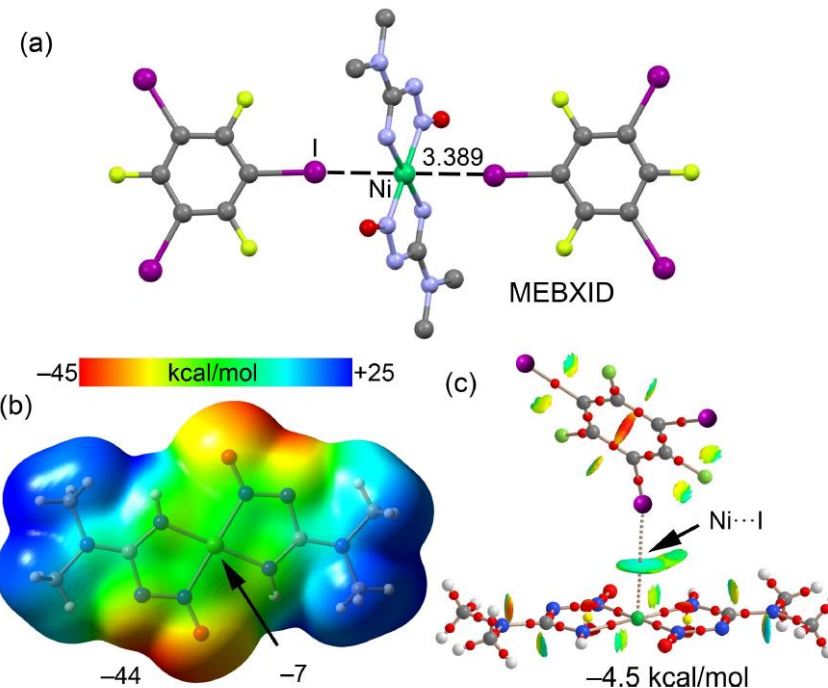
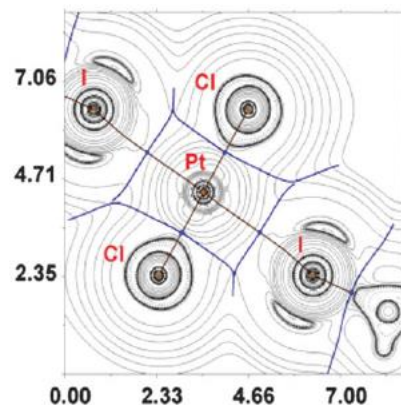
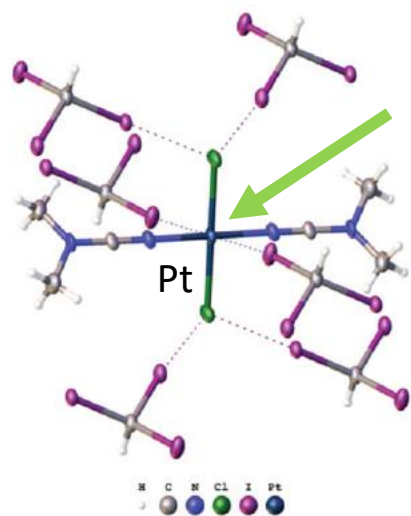
Y. V. Torubaev, I. V. Skabitskiy, *CrystEngComm*, **21** (2019) 7057–7068.

Metaloorganski kokristali

2e)



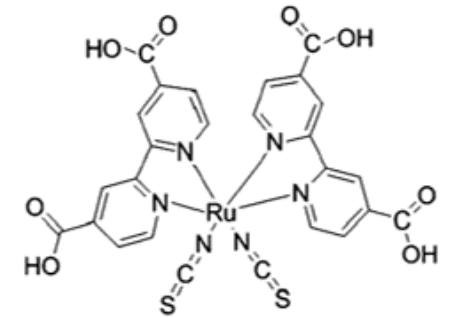
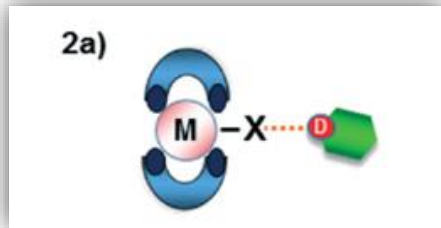
- Nastajanje halogenske veze s metalom prvi puta su opisali Kukushkin i suradnici 2016. godine na kompleksu platine(II).



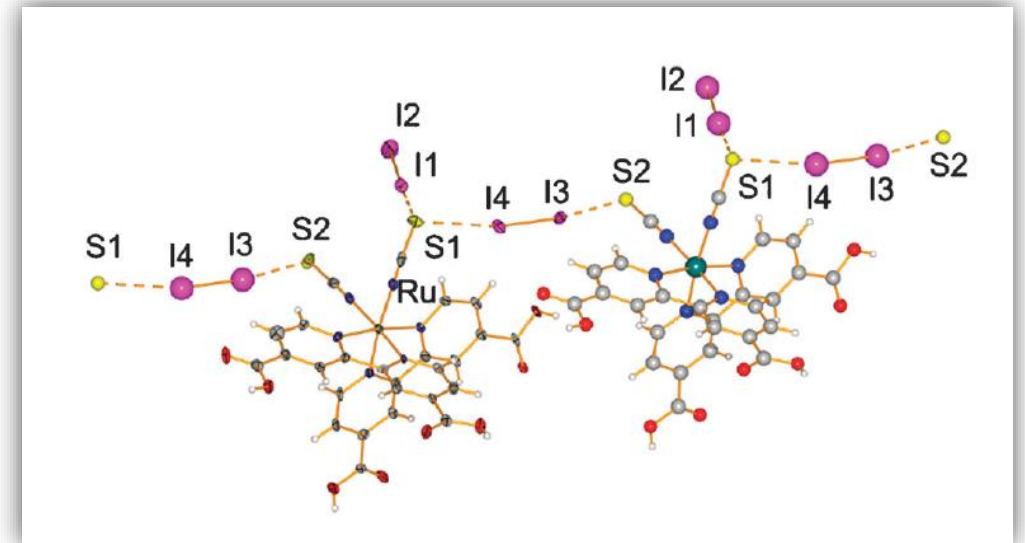
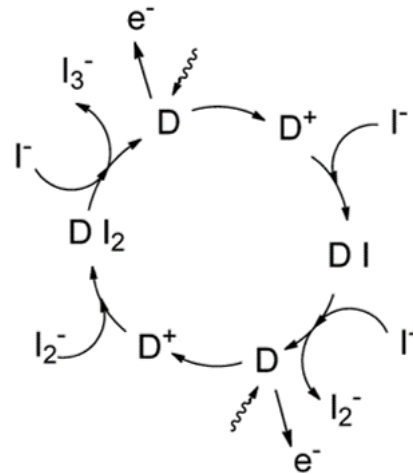
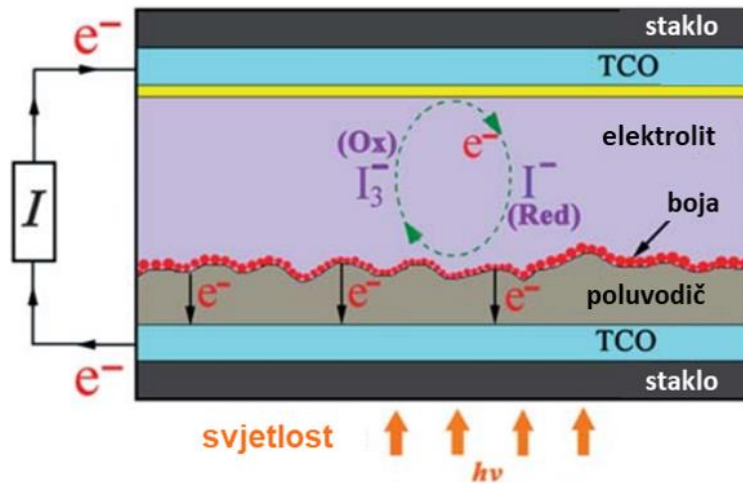
Z. M. Bikbaeva, V. Y. Kukushkin et al., *Inorg. Chem.* **56** (2017) 13562–13578.

D. M. Ivanov, A. S. Novikov, I. V. Ananyev, Y. V. Kirinaand, V. Y. Kukushkin, *Chem. Commun.* **52** (2016) 5565–5568.

Metaloorganski kokristali

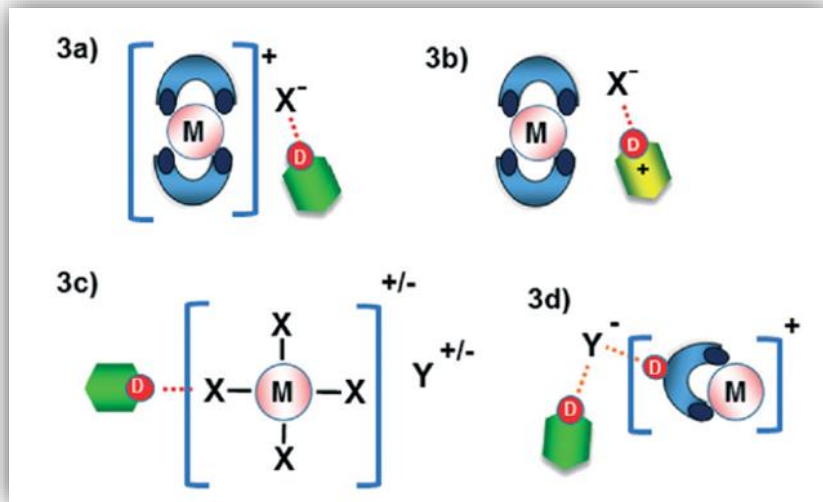


- bojilo u bojom senzibiliziranim solarnim ćelijama
- proces generiranja struje \rightarrow boja se oksidira, a zatim reducira elektrolitom koji je najčešće redoks par I^-/I_3^-



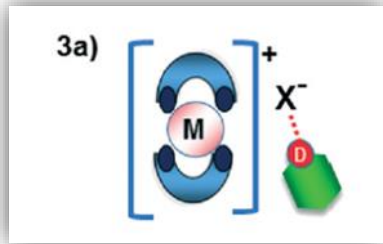
- izoliran međuprodukt reakcije - kokristal

Metaloorganski ionski kokristali

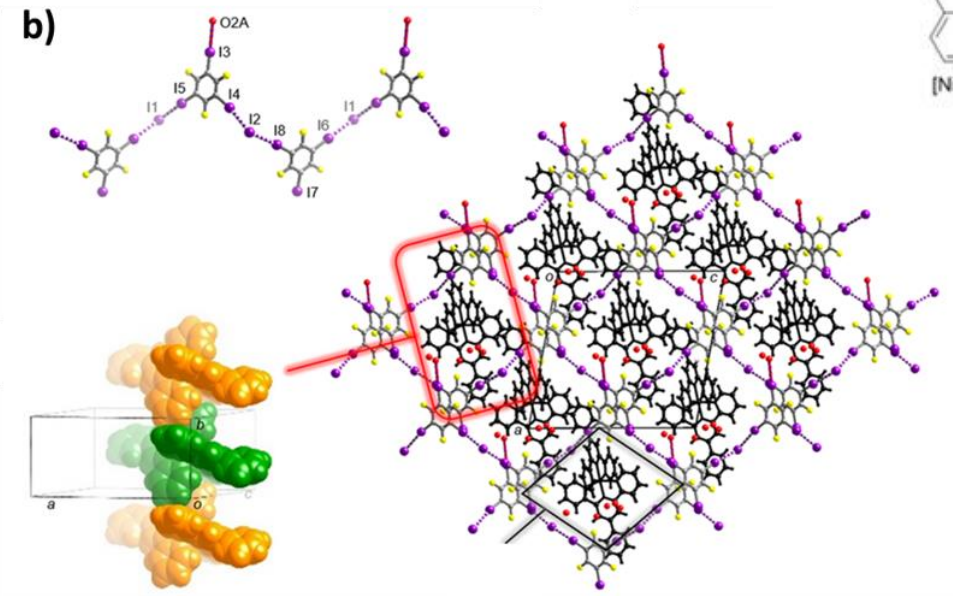
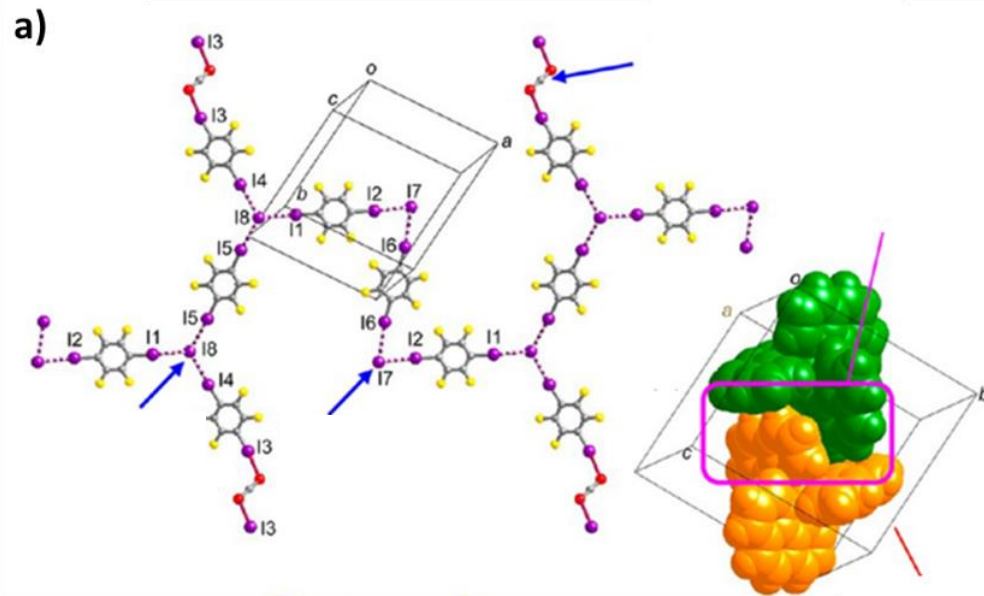
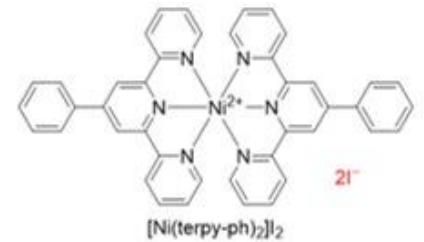


- višekomponentni sustavi kod kojih je barem jedna komponenta ionski spoj
- u odnosu na soli i kokristale, ionski kokristali su značajno manje istraženi
- strategije **3a** i **3c** najviše zastupljene u literaturi

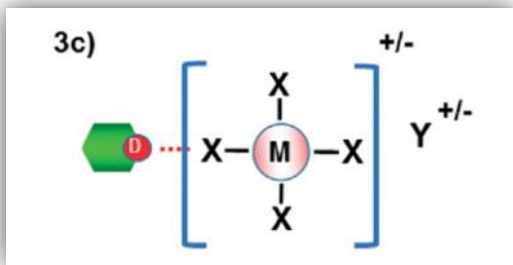
Metaloorganski ionski kokristali



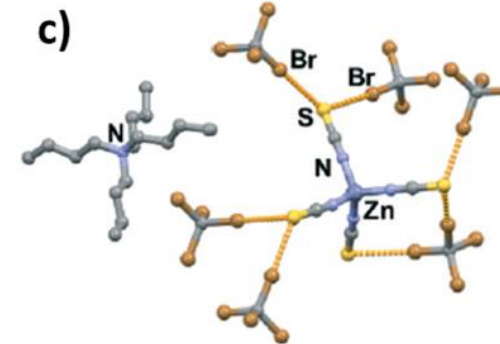
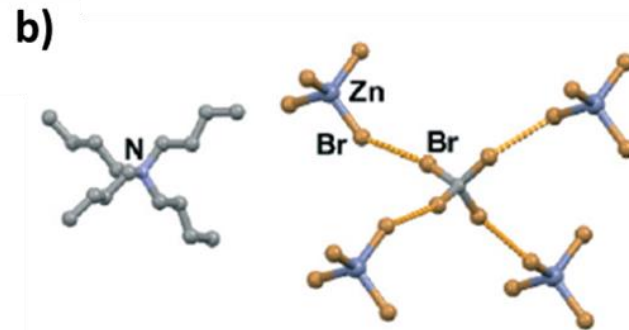
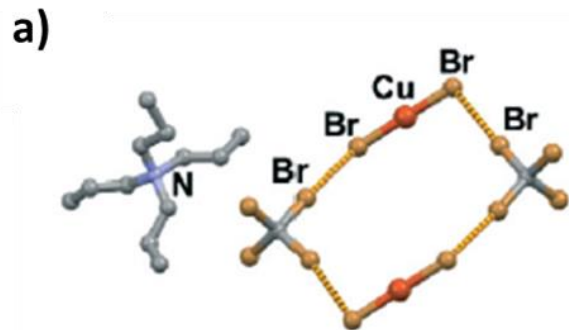
- sistematično istraživanje kokristalizacije kloridnih i jodidnih soli niklovog(II) kompleksa s fenantrolinom te jodidnih soli niklova(II) kompleksa s terpiridinskim ligandima s perhalogeniranim donorima



Metaloorganski ionski kokristali

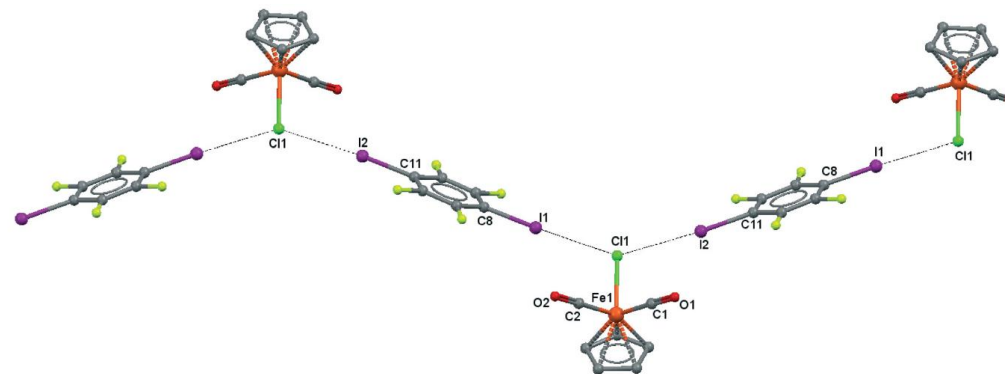
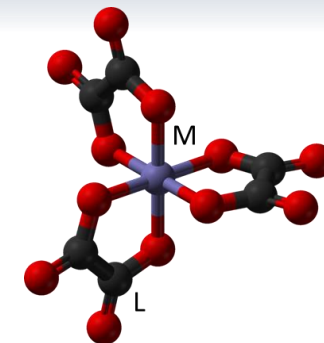


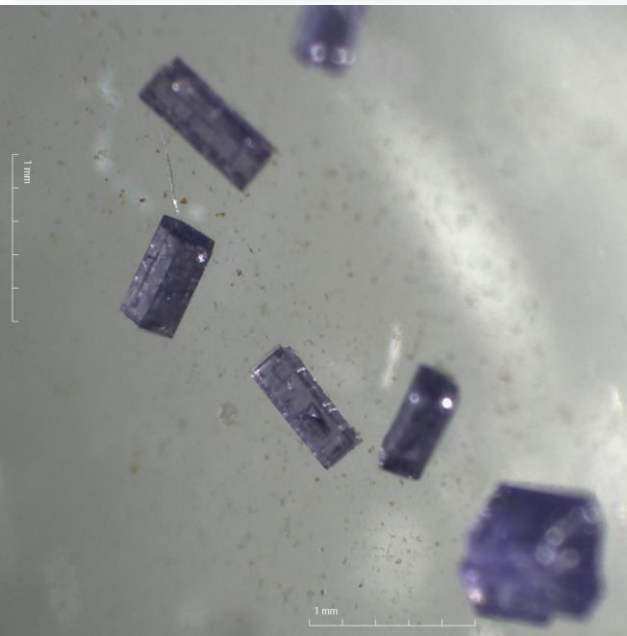
- istraživanje provedeno u ionskim kokristalima s halogenometalnim i pseudohalogenometalnim anionima (CuBr_2^- , ZnBr_4^{2-} , CoBr_4^{2-} , CdBr_4^{2-} , $\text{Pt}_2\text{Br}_6^{2-}$ i $\text{Zn}(\text{NCS})_4^{2-}$)
- mreže povezane halogenskom vezom u kojima su anioni politopični akseptori halogenske veze



Zaključak

- ❑ halogenska veza je vrlo pouzdana međumolekulska interakcija te pruža mnoštvo mogućnosti u dizajnu višekomponentnih metaloorganskih krutina
- ❑ najviše proučavani višekomponentni sustavi su metaloorganske soli, kokristali i ionski kokristali
- ❑ proučavanjem višekomponentnih sustava metaloorganskih spojeva došlo je do novih saznanja o prirodi halogenske veze
- ❑ metaloorganski višekomponentni sustavi pružaju i potencijalnu primjenu u području molekularnih vodiča te su omogućili bolje razumijevanje rada bojom senzibiliranih solarnih ćelija
- ❑ potencijal za daljnja istraživanja





Hvala!

