O‘ZBEKISTON MILLIY UNIVERSITETI HUZURIDAGI
FAN DOKTORI ILMIY DARAJASINI BERUVCHI
DSc.03/30.12.2019.K.01.03 RAQAMLI ILMIY KENGASH

SHAROF RASHIDOV NOMIDAGI SAMARQAND DAVLAT UNIVERSITETI

TOSHPULATOV DOSTON TOLMAS O‘G‘LI

3d-METALLARNING GOMOLEPTIK VA GETEROLEPTIK KOMPLEKS BIRIKMALARI SINTEZI VA FOTOKIMYOVIY TADQIQOTI

02.00.01 – Noorganik kimyo

KIMYO FANLARI BO‘YICHA FALSAFA DOKTORI (PhD)
DISSERTATSIYASI AVTOREFERATI

Toshkent – 2025

UO‘K: 541.49:546.722:546.732:546.742

Kimyo fanlari bo‘yicha falsafa doktori (PhD) dissertatsiyasi avtoreferati mundarijasi

Оглавление автореферата диссертации доктора философии (PhD) по химическим наукам

Contents of dissertation abstract of doctor of philosophy (PhD) on chemical sciences

O‘ZBEKISTON MILLIY UNIVERSITETI HUZURIDAGI
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Kimyo fanlari bo‘yicha falsafa doktori (PhD) dissertatsiyasi mavzusi O‘zbekiston Respublikasi Oliy ta’lim, fan va innovatsiyalar vazirligi huzuridagi Oliy attestatsiya komissiyasida B2021.1.PhD/K380 raqam bilan ro‘yxatga olingan.

Dissertatsiyasi Sharof Rashidov nomidagi Samarqand davlat universitetida bajarilgan.

Dissertatsiya avtoreferati uch tilda (o‘zbek, ingliz, rus (rezyume)) Ilmiy kengashning veb-sahifasida (www.ik-kimyo.nuu.uz) va “Ziyonet” Axborot-ta’lim portalida (www.ziyonet.uz) joylashtirilgan.

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Dissertatsiya himoyasi O‘zbekiston Milliy universiteti huzuridagi DSc. 03/30.12.2019.K.01.03 raqamli Ilmiy kengashning 2025-yil “17” aprel soat 14^{00} dagi majlisida bo‘lib o‘tadi (Manzil: 100174, Toshkent, Universitet ko‘chasi, 4-uy. Tel.: (99871) 227-12-24, faks: (99824) 246-53-21; 246-02-24, e-mail: ilmiy_kengash@nuu.uz).

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Dissertatsiya avtoreferati 2025-yil “04” aprel kuni tarqatildi.
(2025-yil “ 03 ” aprel dagi 12-raqamli reyestr bayonnomasi).

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KIRISH (falsafa doktori (PhD) dissertatsiyasi annotatsiyasi)

Dissertatsiya mavzusining dolzarbligi va zarurati. Dunyoda energiya manbalariga talab oshib borganligidan samaradorligi yuqori va barqaror quyosh elementlari uchun moddalar sintez qilish bugungi kunda juda muhim hisoblanadi. Bunday sensibilizatorlar kelib chiqishiga koʻra oʻta toza kremniyli, noorganik kompleks birikmali va organik birikmali turlarga boʻlinadi. Noorganik kompleks birikmalarni sensibilizatorlar sifatida ishlatish koʻp tomonlama qolgan ikkita muqobiliga nisbatan samarador hisoblanadi. Bundan tashqari zaharli va yuqori konsentratsiyalarda qoʻllaniluvchi birikmalardan voz kechgan holda iqtisodiy tomondan qulay boʻlgan ekologik xavfsiz metall kompleks tipidagi sensibilizatorlarni yaratishga alohida eʼtibor berilmoqda. Jumladan, metall sirtida mustahkam himoya qavati hosil qiluvchi hamda past konsentratsiyalarda va turli harorat intervalida samaradorlikka ega fotosensibilizatorlardan foydalanish muhim oʻrin tutadi.

Jahonda kompleks birikmalar sintezi va ularning turli sohalarda qoʻllanilishi doimo eng muhim yoʻnalishlardan biri boʻlib kelmoqda. Bunday noorganik sensibilizatorlar sifatida koʻpincha ruteniy bipiridin komplekslari ishlatiladi, lekin ruteniy birikmalari nafaqat qimmat, balki zaharli hamdir. Shuning uchun arzonroq va zaharliligi kam metall kompleks birikmalari sintezi va ularni sensibilizatorlarda ishlatish muhim ahamiyat kasb etadi.

Respublikamizda ilgʻor innovatsion texnologiyalarni ishlab chiqish, shuningdek, sanoatni jadal rivojlantirishga alohida eʼtibor qaratilmoqda. Bu borada amalga oshirilgan ishlar doirasida muayyan natijalarga erishilmoqda va ushbu sohada keng koʻlamli tadbirlar amalga oshirilmoqda. Oʻzbekiston Respublikasi Prezidentining 2022-yil 28-yanvardagi PF-60-son “2022-2026-yillarga moʻljallangan Yangi Oʻzbekistonning taraqqiyot strategiyasi toʻgʻrisida”gi Farmonida[1] “mavjud imkoniyatlarni toʻliq ishga solgan holda mahalliy sanoat tarmoqlari eksport salohiyatini yanada rivojlantirish”ga yoʻnaltirilgan muhim vazifalar belgilab berilgan. Bu borada, Fe(II), Co(II), Ni(II) ionlarining organik ligandlar ishtirokida 6,6 – disiano-2,2-bipiridin, 3,8-dibromo-1,10-fenantrolin, 2,2-bixinolin, 3,4,7,8-tetrametil-1,10-fenantrolin hosil qilgan kompleks birikmalaridan boʻyoq sezgir boʻlgan quyosh elementlari sifatida foydalanish muhim ahamiyat kasb etadi.

Oʻzbekiston Respublikasi Prezidentining 2022-yil 28-yanvardagi “2022-2026-yillarga moʻljallangan Yangi Oʻzbekistonning taraqqiyot strategiyasi toʻgʻrisida”gi PF-60-son Farmonida, 2018-yil 25-oktyabrdagi “Oʻzbekiston Respublikasida kimyo sanoatini jadal rivojlantirish chora-tadbirlari toʻgʻrisida”gi PQ-3983-son, 2019-yil 3-apreldagi “Kimyo sanoatini yanada isloh qilish va uning investitsiyaviy jozibadorligini oshirish chora-tadbirlar toʻgʻrisida”gi PQ-4265-son, 2021-yil 13-fevraldagi “Kimyo sanoati korxonalarini yanada isloh qilish va moliyaviy sogʻlomlashtirish, yuqori qoʻshilgan qiymatli kimyoviy mahsulotlar ishlab chiqarishni rivojlantirish chora-tadbirlari toʻgʻrisida”gi PQ-4992-son Qarori

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[1] Oʻzbekiston Respublikasi Prezidentining 2022 yil 28 yanvardagi PF-60-son “2022-2026 yillarga moʻljallangan Yangi Oʻzbekistonning taraqqiyot strategiyasi toʻgʻrisida”gi Farmoni.

hamda mazkur faoliyatga tegishli boshqa me’yoriy-huquqiy hujjatlarda belgilangan vazifalarni amalga oshirishda ushbu dissertatsiya tadqiqoti natijalari muayyan darajada xizmat qiladi.

Tadqiqotning Respublika fan va texnologiyalari rivojlanishining ustuvor yo‘nalishlariga mosligi. Mazkur tadqiqot Respublika fan va texnologiyalar rivojlanishining VII. “Kimyo texnologiyalari va nanotexnologiya” ustuvor yo‘nalishlariga muvofiq bajarilgan.

Muammoning o‘rganilganlik darajasi. Dunyoda olimlar tomonidan olib borilayotgan ko‘pgina ilmiy tadqiqot ishlari noorganik kompleks birikmalarga asoslangan sensibilizatorlar bo‘lib, Respublikamizda yangi yo‘nalishlardan hisoblanadi. Bu sohada AQSh Berkli universiteti professori M.Gratsel va B.Oregan, Massey universiteti (Yangi Zelandiya) professori U.Kampbell, Michigan universiteti (AQSh) professori M.Shtayn, Lill universiteti (Fransiya) professori M.Sliva va boshqalar ilmiy tadqiqot ishlari olib borishgan.

Hozirgi kunda sintez qilingan kompleks birikmalardan bo‘yoq sezgir quyosh elementlari sifatida ishlatish bo‘yicha katta hajmdagi nazariy va amaliy ma’lumotlar to‘plangan. Bu borada G.Boschloo, I.Benesperi, J.Xavier, L.Gibson, M. Pavone, H.Pettersson, A. Hagfeldt, M. Freitag kabi olimlarning izlanishlari alohida e’tiborga loyiqdir.

Mamlakatimizda kompleks birikmalarning sintezi, tuzilishi, xossalari va tadqiqoti bo‘yicha N.A.Parpiyev, B.T.Ibragimov, T.A.Azizov, X.T.Sharipov, A.A.Shabilolov, X.X.Turayev, B.B.Umarov, Sh.A.Kadirova, J.M.Ashurov, A.B.Ibragimov, Sh.Sh.Daminova va ularning shogirdlari katta hissa qo‘shishgan. Shu bilan birgalikda, adabiyotlar tahlilining ko‘rsatishicha, 3d metall tuzlarining organik ligandlar bilan hosil qilgan komplekslarini tahlil qilish bo‘yicha keng miqyosda tajriba natijalari bo‘lishiga qaramasdan, Fe(II), Co(II), Ni(II) ionlarining organik ligandlar ishtirokida hosil qilgan kompleks birikmalaridan bo‘yoq sezgir bo‘lgan quyosh elementlari sifatida foydalanish yetarli darajada o‘rganilmagan. Shu sababli, Fe(II) ionining 3,4,7,8-tetrametil-1,10-fenantrolin, 6,6 – disiano-2,2-bipiridin ligandlari bilan hosil qilgan kompleks birikmalarni sintez qilish, fizik-kimyoviy xossalarini o‘rganish va ulardan sensibilizatorlar sifatida foydalanish alohida ilmiy qiziqish kasb etadi.

Dissertatsiya tadqiqotining dissertatsiya bajarilgan oliy ta’lim muassasasining ilmiy tadqiqot ishlari rejalari bilan bog‘liqligi. Dissertatsiya tadqiqoti Sharof Rashidov nomidagi Samarqand davlat universiteti Noorganik kimyo va materialshunoslik kafedrasi ilmiy yo‘nalishiga muvofiq bajarilgan.

Tadqiqotning maqsadi. Fe(II), Co(II), Ni(II) ionlarining organik ligandlar ishtirokida hosil qilgan gomoleptik va geteroleptik kompleks birikmalari sintezini amalga oshirish hamda olingan birikmalarning fotokimyoviy xossalarini o‘rganishdan iborat.

Tadqiqotning vazifalari. Fe(II), Co(II), Ni(II) ionlarining organik ligandlar bilan gomoleptik va geteroleptik kompleks birikmalari sintez jarayonining maqbul sharoitlarini aniqlash;

3d-metallarning fenontrolin va bipiridin hosilalari bilan komplekslarining elektron tuzilishi, energetik va geometrik parametrlari hamda reaksion qobiliyatini zamonaviy kvant-kimyoviy usullar yordamida hisoblash;

sintez qilingan gomoleptik va geteroleptik kompleks birikmalarining tuzilishi va xossalarini zamonaviy fizik-kimyoviy usullar yordamida tahlil qilish;

sintez qilingan kompleks birikmalarning termodinamik va eritmadagi barqarorlik konstantalarini aniqlash;

olingan kompleks birikmalardan bo‘yoq sezgir quyosh elementi sifatida foydalanish hamda fotosensibilizator sifatida tadqiq etish.

Tadqiqotning ob’yekti. 2,2-bipiridin va 1,10-fenantrolin hosilalari, ularning Fe(II), Co(II), Ni(II) tuzlari bilan kompleks birikmalari, ZnO hamda FTO shisha hisoblanadi.

Tadqiqotning predmeti. Gomoleptik va geteroleptik kompleks birikmalarining tarkibi, tuzilishi, individualligi, fizik-kimyoviy, fotosensibilizatorlik xossalarini o‘rganish hisoblanadi.

Tadqiqotning usullari. Infraqizil spektroskopiyasi(IQ), elektron yutilish spektroskopiyasi (UV-vis), diffuz aks etrish spektroskopiyasi, Raman spektroskopiyasi, kukun rentgen difraksiyasi (XRD), statsionar lyumenessensiya, vaqtga bog‘liq lyuminessensiya, elektron paramagnit rezonansi (EPR) spektroskopiya, differensial-termik analiz (DTA) zamonaviy kvant-kimyoviy hisoblashlar hamda solishtirma qarshilik, kuchlanish va tok kuchi qiymatlarini aniqlash kabi zamonaviy tadqiqot usullaridan foydalanilgan.

Tadqiqotning ilmiy yangiligi quyidagilardan iborat:

Fe(II), Co(II), Ni(II) ionlarining organik ligandlar (6,6–disiano-2,2-bipiridin, 3,8-dibromo-1,10-fenantrolin, 2,2-bixinolin, 3,4,7,8-tetrametil- 1,10-fenantrolin) qo‘shimcha suvli va spirt molekulalari ishtirokida 32 ta yangi gomoleptik va geteroleptik komplekslari sintez qilingan;

Fe(II) ionlarining 2,2-bipiridin, 6,6–disiano-2,2-bipiridin, 3,4,7,8-tetrametil-1,10-fenantrolin ishtirokida eritmada hosil qilingan gomoligandli komplekslarning barqarorlik konstanta qiymatlari va ularni ligandlar tabiatiga bog‘liqligi aniqlangan;

kvant-kimyoviy usullarning takomillashtirilgan dasturlaridan foydalanib, sintez qilingan kompleks molekulalarning geometrik va energetik parametrlari, atomlardagi zaryadlarning taqsimoti, reaksion markazlari aniqlangan;

sintez qilingan komplekslarning termik xossalari, termik parchalanish mexanizmi va ularning miqdoriy, energetik jihatlari hamda DSC natijalaridan foydalanib ayni jarayonlar uchun entalpiya o‘zgarishi aniqlangan;

sintez qilingan kompleksning elektron o‘tish energiyasini Taus usuli bilan har ikkala $(\alpha h\nu)^2$ va $(\alpha h\nu)^{1/2}$ holatlar uchun hisoblanib, yarimo‘tkazgich tabiati orqali BSQElar sensibilizator uchun mos kelishi asoslangan;

sintez qilingan tarkibida Fe(II) ionlari gomo- va geteroligandli komplekslarning fotosensibilizatorlik xususiyati AM1.5G simulyatoridan foydalanilganda 5,72% - 6,14 % tashkil qilsa, tabiiy quyosh nurlarida esa 11% – 12% gacha yetishi aniqlandi.

Tadqiqotning amaliy natijalari quyidagilardan iborat:

Fe(II), Co(II), Ni(II) ionlarining organik ligandlar ishtirokida (6,6 – disiano-2,2-bipiridin, 3,8-dibromo-1,10-fenantrolin, 2,2-bixinolin, 3,4,7,8-tetrametil-1,10-fenantrolin) kompleks birikmalar sintez qilishning optimal sharoitlari aniqlangan;

sintez qilingan yangi komplekslarning vaqtga bog‘liq fluoressent spektr tahlili asosida asetonitril eritmasidagi yashash davri 7-10 ns ekaniligi aniqlangan.

sintez qilingan yangi kompleks birikmalardan bo‘yoqlarga sezgir bo‘lgan quyosh elementi sifatida ishlashini baholashda fill faktor(FF) 0,6-0,65 qiymat oralig‘ida bo‘lishi aniqlandi.

Fe(II), Co(II), Ni(II) ionlarining 2,2-bipiridin va 1,10-fenantrolin hosilalari bilan eritmada hosil qilgan komplekslari bo‘yoq sezgir bo‘lgan quyosh elementlari uchun qo‘llanilganda bo‘yoq moddalar fotosensibilizatorlik hamda yuqori assimilyatsiya koeffitsiyentiga ega ekanligi bois foydali ish koeffitsiyentini 5,72 – 6,14% ni tashkil qilishi aniqlangan.

2,2-bipiridin va 1,10-fenantrolin hosilalari, ularning Fe(II), Co(II), Ni(II) ionlari bilan hosil qilgan kompleks birikmalari BSQE sifatida tavsiya qilingan.

Tadqiqot natijalarining ishonchliligi. Infraqizil spektroskopiyasi (IQ), elektron yutilish spektroskopiyasi (UV-vis), diffuz aks ettirish spektroskopiyasi, Raman spektroskopiyasi, kukun rentgen difraksiyasi (XRD), statsionar lyumenessensiya, vaqtga bog‘liq lyuminessensiya, elektron paramagnit rezonansi (EPR) spektroskopiya, differensial-termik analiz (DTA) zamonaviy kvant-kimyoviy hisoblashlar hamda solishtirma qarshilik, kuchlanish va tok kuchi qiymatlarini aniqlash kabi zamonaviy tadqiqot usullari bilan asoslangan.

Tadqiqot natijalarining ilmiy va amaliy ahamiyati.

Tadqiqot natijalarining ilmiy ahamiyati Fe(II), Co(II), Ni(II) ionlarining organik ligandli komplekslari to‘g‘risidagi ilmiy adabiyotlarni monitoringi, yangi sintez qilingan komplekslarning tarkibi, tuzilishi, donor atomlari koordinatsiyalanishini, barqarorlik konstantalari, fizik-kimyoviy tahlil usullarda tadqiq qilish, $[M(N)_3]$ tarkibli komplekslarning fotosensibilizatorlik xususiyatlari, solishtirma qarshilik, kuchlanish va tok kuchi kabi elektrokimyoviy parametrlarini aniqlash bilan izohlanadi.

Tadqiqot natijalarining ahamiyati yangi kompleks birikmalar sintezi va qattiq holda ajratib olish usullarini ishlab chiqishga, yarimo‘tkazgichlik va optik xossalarni namoyon qilishi natijasida quyosh nurlariga sezgir bo‘yoq moddalar asosida ishlaydigan quyosh elementlarida foydalanishga xizmat qiladi.

Tadqiqot natijalarining joriy qilinishi. Quyosh elementlari uchun noorganik kompleks birikmalar olish bo‘yicha olingan ilmiy natijalar asosida:

“Elektrokimyozavod” qo‘shma korxonasi aksiyadorlik jamiyati qoshidagi “ELKIMYO–AGROHIMOYA” MChJ da amaliyotga joriy etildi (“Elektrokimyozavod” QK AJ ning 2024-yil 6-maydagi №92 sonli ma’lumotnomasi). 2,2-bipiridin va 1,10-fenantrolin hosilalari bilan tarkibidagi Fe^{2+}, Co^{2+}, Ni^{2+} ionlarini bilan rangli komplekslar hosil qildi, bunda 3d metall ionlarining 0,0025 mol/l gacha past konsentratsiyalarda maqsadli molekulalar mavjudligini aniqlash imkonini bergan. “Elektrokimyozavod” QK AJ ning 2026-2028 yillardagi innovatsion rivojlanitrish dasturiga kiritilgan;

“BMAX BUILDING MATERIALS” MChJ qo‘shma korxonasida amaliyotga joriy etildi (“BMAX BUILDING MATERIALS” MCHJ ning 2024-yil 5-apreldagi №74/A sonli ma’lumotnomasi). Fe(II) ionining 3 ta gomoleptik 4 ta geteroleptik; Co(II) ionining 5 ta gomoleptik 8 ta geteroleptik; Ni(II) ionining 5 ta gomoleptik

7 ta geteroleptik komplekslari bo‘yoq sezgir bo‘lgan quyosh elementlari uchun qo‘llanilganda bo‘yoq moddalar fotosensibilizatorlik hamda yuqori assimilyatsiya koeffitsiyentiga ega ekanligi aniqlangan.

Rossiya Fedratsiyasining “FLUID” MChJ da amaliyotga joriy etildi (“FLUID” MChJ ning 2024-yil 3-apreldagi №94 sonli ma’lumotnomasi). 3d-metallarning gomoleptik $[Fe(L_1)_3](PF_6)_2$, $[Co(L_1)_3](PF_6)_2$, $[Ni(L_1)_3](PF_6)_2$, $[Fe(L_4)_3](PF_6)_2$, $[Co(L_4)_3](PF_6)_2$, $[Ni(L_4)_3](PF_6)_2$; geteroleptik $[Co(L_1)(L_2)_2](PF_6)_2$, $[Fe(L_4)_2(L_1)](PF_6)_2$, $[Co(L_1)(L_4)_2](PF_6)_2$, $[Ni(L_1)(L_4)_2](PF_6)_2$, $[Ni(L_1)(L_2)_2](PF_6)_2$, $[Ni(L_1)_2(L_4)](PF_6)_2$ komplekslari bo‘yoq sezgir bo‘lgan quyosh elementlari uchun qo‘llanildi hamda bo‘yoq moddalar fotosensibilizatorlik hamda yuqori assimilyatsiya koeffitsiyentiga ega ekanligi aniqlangan.

Tadqiqot natijalarining aprobatsiyasi. Ushbu tadqiqot natijalari 16 ta, jumladan 5 ta xalqaro va 11 ta Respublika ilmiy-amaliy anjumanlarida ma’ruza qilingan va muhokamadan o’tkazilgan.

Tadqiqot natijalarining e’lon qilinganligi. Dissertatsiya mavzusi bo‘yicha jami 23 ta ilmiy ishlar chop etilgan, shulardan O‘zbekiston Resspublikasi Oliy attestatsiya komissiyasining falsafa doktori (PhD) dissertatsiyalari asosiy ilmiy natijalarini chop etish tavsiya etilgan ilmiy nashrlarida 7 ta maqola, shu jumladan 5 ta maqola respublika va 2 maqola xorijiy jurnallarda va xalqaro ilmiy anjumanlarda 5 ta, respublika ilmiy amaliy konferensiyalarida 10 ta tezislar nashr etilgan.

Dissertatsiyaning tuzilishi va hajmi. dissertatsiya tarkibiga kirish, to‘rtta bob, xulosalar, foydalanilgan adabiyotlar ro‘yxati va ilovalardan iborat. Dissertatsiyaning hajmi 120 bet.[2]

DISSERTATSIYANING ASOSIY MAZMUNI

Kirish qismida o‘tkazilgan tadqiqotlarning dolzarbligi va zarurati asoslangan, maqsad va vazifalari keltirilgan, obyekti va predmeti tavsiflangan, tadqiqotning respublika fani va texnologiyasi rivojlanishining ustuvor yo‘nalishlariga mos kelishi ko‘rsatilgan, tadqiqot natijalarining ilmiy yangiligi, ilmiy va amaliy ahamiyati bayon qilingan, olingan natijalarning ilmiy va amaliy ahamiyati, ishonchliligi, ularning amaliyotga tatbiq qilinishi ochib berilgan va chop etilgan ishlar hamda dissertatsiya tuzilishi bo‘yicha ma’lumotlar keltirilgan.

Dissertatsiyaning **“Fotosensibilizatorlar turlari va 3d metall komplekslarining bo‘yoq sezgir quyosh elementlarida qo‘llanilish istiqbollari”** deb nomlangan **birinchi bobda** Fe(II), Co(II), Ni(II) ionlarining 2,2-bipiridin va 1,10-fenantrolin hosilalari va ular ishtirokidagi kompleks birikmalari sintezi, fizik-kimyoviy xossalari, tuzilishi, fotosensibilizatorlik xususiyati bo‘yicha adabiyotlardagi ma’lumotlar tahlil qilish asosida dissertatsiya ishining maqsadi va vazifalari asoslangan.

Dissertatsiyaning **“3d (Fe^{2+}, Co^{2+}, Ni^{2+}) metallarining kompleks birikmalari sintezi va tadqiqot usullari”** deb nomlangan **ikkinchi bobda**

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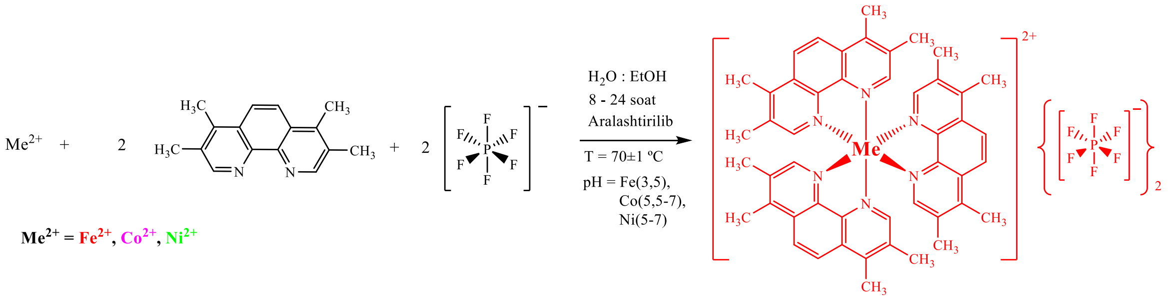
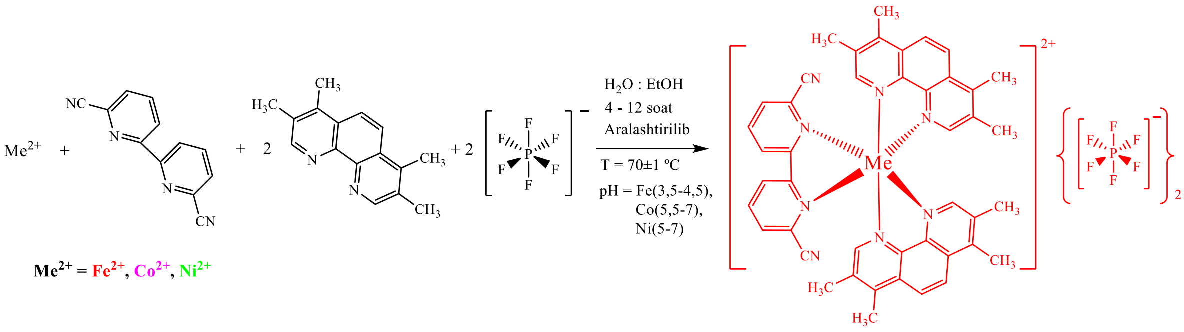
[2] Kimyo fanlari nomzodi, dotsent X.Sh.Tashpulatovga dissertatsiya ishini bajarishda bergan ilmiy maslahatlari uchun minnatdorlik bildiraman.

eritmada kompleks birikmalar hosil bo‘lishini o‘rganish, kompleks birikmalarning sintezi va tuzilishini aniqlashning infraqizil spektroskopiyasi, elektron yutilish spektroskopiyasi, diffuz aks etrish spektroskopiyasi, Raman spektroskopiyasi, kukun rentgen difraksiyasi, statsionar lyumenessensiya, vaqtga bog‘liq lyuminessensiya, elektron paramagnit rezonansi spektroskopiya, differensial-termik analiz, kvant-kimyoviy hisoblashlar hamda solishtirma qarshilik, kuchlanish va tok kuchi qiymatlarini aniqlash kabi zamonaviy tadqiqot usullari haqida ma’lumotlar keltirilgan.

3*d* metallarning organik ligandlar bilan kompleks hosil qilishi bir qancha adabiyotlardan o‘rganilib chiqilib, sintez qilish uchun maqbul sharoitlari tanlab olindi. Tanlab olingan sharoitlar asosida temir, kobalt hamda nikel ionlarining 6,6 –disiano-2,2-bipiridin, 3,8-dibromo-1,10-fenantrolin, 2,2-bixinolin, 3,4,7,8-tetrametil-1,10-fenantrolin ligandlari o‘zaro reaksiyaga kirishib kompleks hosil bo‘lishi, hamda uni cho‘kitrish jarayoni hamda moddani toza holda ajratib olish jarayoni adabiyotlardan o‘rganilib, ba’zi o‘zgartirishlar kiritilgan holda sintez qilish sxemasi taklif qilindi.



1-sxema. Monoligandli komplekslar hosil bo‘lishi



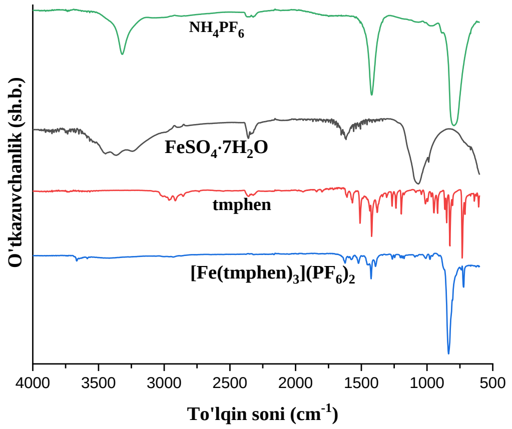
2-sxema. Aralash ligandli komplekslar hosil bo‘lishi

Asosiy ligandlar 3,4,7,8-tetrametil-1,10-fenantrolin (tmphen) va 6,6–disiano-2,2-bipiridin (dcbyp) larning Fe^{2+}, Co^{2+}, Ni^{2+} ionlari bilan gomo- va getroligandli kompleks birikmalarni sintez qilish uchun Me^{2+}: L=1:3 mol nisbatda olinib, 2 mol cho‘ktiruvchi sifatida NH_4PF_6 ishlatildi. Ammoniy geksaftorofosfat kompleks birikmalar sintezida kuchsiz kompleks hosil qiluvchi anioni PF_6^- manbai sifatida ishlatildi, bu modda o‘zining inertligi va ma’lum metall komplekslarini barqarorlashtirish qobiliyati tufayli tadqiqoda foydalanildi. Kompleks birikmlarni eritmada sintez qilishda kuchsiz kislotalidan neytral muhit talab qilinib, 60 °C dan 80 °C haroratlarda oralig‘ida kompleks hosil bo‘lishiga erishilgan, lekin har bir kompleksni sintez qilish uchun alohida pH va harorat talab qilinadi.

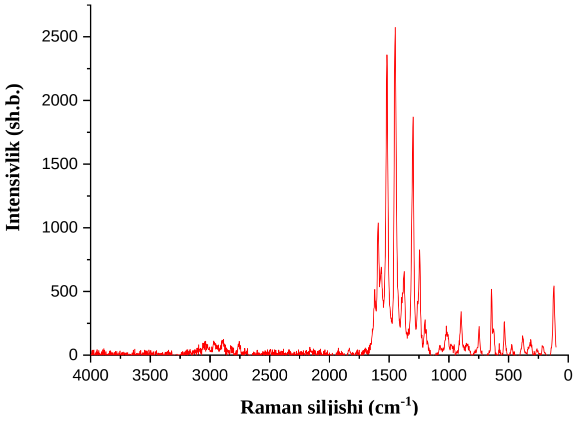
“3d (Fe^{2+}, Co^{2+}, Ni^{2+}) metallar gomoleptik va geteroleptek komplekslarining fizik-kimyoviy tadqiqotlari” deb nomlangan **uchinchi bobda**

sintez qilingan kompleks birikmalarning tuzilishi va fizik-kimyoviy xossalarini o‘rganish natijalari keltirilgan.

Sintez qilingan kompleksning va prekursorlarning FTIQ spektri 1-rasmda keltirilgan. Spektrdan ko‘rinib turibdiki, $[Fe(tmphen)_3](PF_6)_2$ funksional guruh sohasi deyarli bo‘sh (ko‘k chiziq). Yutilish polosalarining birinchi guruhi 1400-1700 cm^{-1} oralig‘ida joylashgan va ular tetrametilfenantrolin ligandi aromatik halqasining valent tebranishlariga tegishli hisoblanadi, ya’ni, C=N valent tebranish polosasi 1596 cm^{-1} da va C=C valent tebranish polosasi 1574 cm^{-1} da namoyon bo‘ldi. O‘rtacha intensivlikdagi tor o‘tkir polosa 720 cm^{-1} da ko‘rinadi va u C–H guruhi valent tebranishiga xosdir. Tebranishlarning ikkinchi guruhi esa 870 cm^{-1} atrofida joylashgan va u geksaftorofosfat anioni valent tebranishlariga mos hisoblanadi. Tebranish polosalaridagi quyidagi siljishlar kompleks hosil bo‘lishida koordinatsion bog‘ azot atomi (donor) bilan temir(II) ioni (akseptor) orasida hosil bo‘lishini ko‘rsatadi. Ya’ni, C=N bog‘i valent tebranish chastotasi 1612 cm^{-1} dan 1596 cm^{-1} ga siljiganda, fenantrolin aromatik halqasi C=C valent tebranish chastotasi 1565 cm^{-1} dan 1574 cm^{-1} gacha siljiydi.



1-rasm. $[Fe(tmphen)_3](PF_6)_2$ kompleksi va prekursorlarining FTIQ spektri.



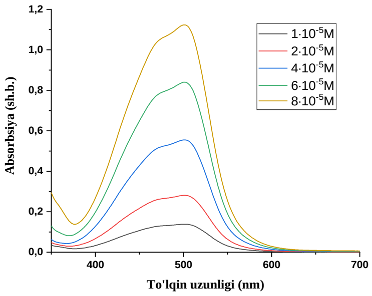
2-rasm. $[Fe(tmphen)_3](PF_6)_2$ kompleksining kombinatsion sochilish (Raman) spektri.

$[Fe(tmphen)_3](PF_6)_2$ kompleksining kombinatsion sochilish (Raman) spektri 2-rasmda keltirilgan va u 1-rasmdagi IQ spektriga komplementar hisoblanadi. Ayni spektrdagi asosiy tebranish polosalari 2000 cm^{-1} dan quyida joylashgan. Namunaning Raman spektridagi asosiy kuchli va o‘tkir polosalar 1511, 1446 hamda 1300 cm^{-1} da joylashgan va fenantrolin aromatik halqasining simmetrik valent tebranishiga tegishli hisoblanadi. 630 cm^{-1} dagi kuchsiz Raman signali esa geksaftorofosfat anionining P–F valent tebranishlariga tegishlidir.

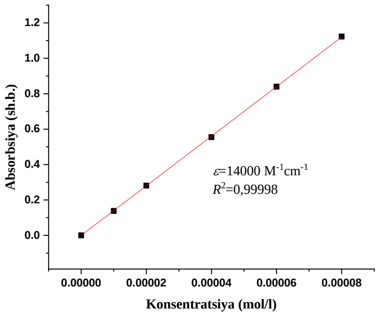
Ayni tadqiqot uchun sintez qilingan $[Fe(tmphen)_3](PF_6)_2$ kompleksi qutbsizdan qutbligacha bo‘lgan turli erituvchilar: dimetilsulfoksid, dimetilformamid, tetragidrofuran, atseton va atsetonitrilda eritilib tadqiqotlar olib borildi. Bunda atsetonitril eng mos erituvchi sifatida tanlandi va kompleksning o‘ziga xos fotofizikaviy xossalari o‘rganildi. Qolgan erituvchilarda kompleks beqaror yoki fluoressensiya xossalarini namoyon qilmadi. Bunga nurlanishsiz relaksatsiya jarayonlarining tezligi kattaligi sabab bo‘ladi.

Kompleksning optik xossalari ularning elektron tuzilishi va ular orasidagi o‘tishlarga bog‘liq. Elektron o‘tish tanlash qoidasi bilan ruxsat berilgan bo‘lsa, uning amalga oshish ehtimoli shuncha katta va shunga mos ε qiymati ham katta bo‘ladi. Ma’lumki, *d*-metallar kompleks birikmalari uchun 3 xil tanlash qoidasi amal qiladi. Bular Laporta, spin va juftlik tanlash qoidalari bo‘lib, biror kompleksning molyar ekstinksiya koeffitsiyenti qiymatiga qarab unda qanday o‘tishlarga ruxsat berilgan yoki ta’qiqlanganligini empirik baholash mumkin.

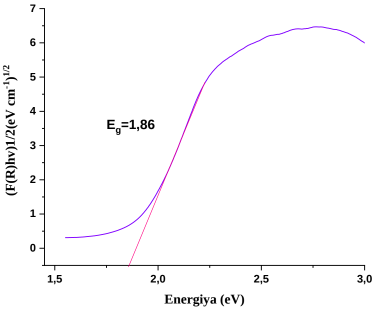
BSQE maqsadida sensibilizator yoki mediator sifatida ishlatishga mos kelishi uchun kompleksning molyar yutilish (ekstinksiya) koeffitsiyenti yuqori bo‘lishi kerak. Shuning uchun $[Fe(tmphen)_3](PF_6)_2$ kompleksining $1\cdot10^{-5}$ M dan $8\cdot10^{-5}$ M gacha konsentratsiyali eritmalari tayyorlanib, 500 nm dagi optik zichligi o‘lchandi (3-rasm).



3-rasm. $[Fe(tmphen)_3](PF_6)_2$ kompleksining atsetonitrilda turli xil konsentratsiyadagi ertitmasining elektron yutilish spektri



4-rasm. $[Fe(tmphen)_3](PF_6)_2$ kompleksining atsetonitril eritmasida graduirovka chizig‘i

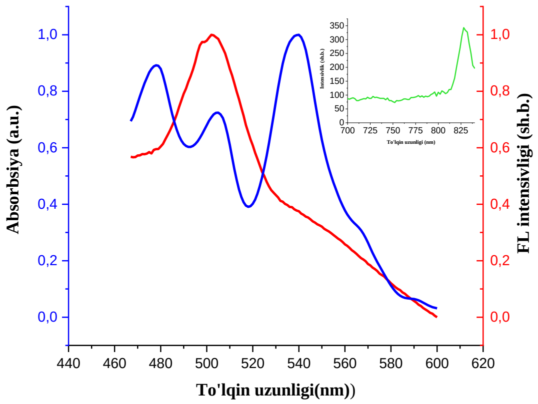


5-rasm. $[Fe(tmphen)_3](PF_6)_2$ kompleksining Taus diagrammasi

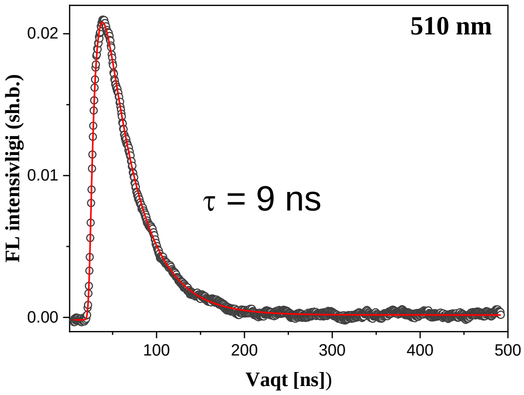
Spektrdan sintez qilingan kompleksning nurni yaxshi yutishini juda past konsentratsiyada ham sezilarli optik zichlik namoyon qilishidan bilish mumkin. 500 nm dagi optik zichlik qiymatlari bilan konsentratsiya orasidagi bog‘liqligidan foydalanib $[Fe(tmphen)_3](PF_6)_2$ kompleksining molyar ekstinksiya koeffitsiyenti hisoblandi (4-rasm). Ushbu bog‘liqlikdan kompleksning molyar ekstinksiya koeffitsiyenti 14000 $M^{-1}\cdot cm^{-1}$ atrofida ekanligi kelib chiqdi. Bunday yetarlicha katta molyar ekstinksiya koeffitsiyenti qiymati ayni kompleksda barcha o‘tishlar ruxsat berilganligini ko‘rsatdi. $[Fe(tmphen)_3](PF_6)_2$ kompleksi elektron yutilish spektridagi polosalar tabiatini yanada yaxshiroq tushunish uchun Tanabe-Sugano diagrammasiga murojaat qilsak, 500 nm dagi polosa $^1A_1 \rightarrow {}^1T_1$ hamda $^1A_1 \rightarrow {}^1T_2$ o‘tishlardan kelib chiqqan deb xulosa qilish mumkin.

$[Fe(tmphen)_3](PF_6)_2$ kompleksining yarimo‘tkazgich tabiatini baholash uchun Taus usulidan foydalanib to‘g‘ri va teskari ta’qiqlangan zona energiyasi (kengligi) hisoblandi (5-rasm). Teskari ta’qiqlangan zona energiyasi $E = (\alpha h\nu)^{1/2}$ tenglama bilan hisoblanib, ekstrapolyatsiya qilinganda energiya darajasi 1,86 eV ekanligi aniqlandi. Kompleksning hisoblangan yarimo‘tkazgich tabiati uning BSQE uchun sensibilizator sifatida mos kelishini tasdiqlaydi.

$[Fe(tmphen)_3]^{2+}$ ning atsetonitrildagi absorbsiya va emission spektrlari 6-rasmda keltirilgan. Uning elektron yutilish spektridagi 480, 510 va 540 nm dagi polosalar yaqqol ajralib turadi (ko‘k chiziq). Shuningdek, ushbu spektrda 570 va 590 nm da ham qo‘shimcha kuchsiz polosalar ham borligini ko‘rish mumkin. Ayni kompleksning emission spektri esa bir keng polosaga ega bo‘lib, asosiy polosa namuna 440 nm da, qo‘zg‘atilganda 510 nm da emission maksimumni namoyon qiladi (qizil chiziq).



6-rasm. $[Fe(tmphen)_3]^{2+}$ kompleksining atsetonitrildagi absorbsiya (ko‘k chiziq) va emission (qizil chiziq) spektlari; λ_{exc} = 440 nm. Rasm ichidagi spektrda yashil chiziq bilan berilgan emission spekt uchun λ_{exc} = 540 nm ga teng



7-rasm. $[Fe(tmphen)_3]^{2+}$ kompleksining atsetonitrildagi fluoressensiya yashash davri spektri

Moddaning 510 nm dagi emission spektrning vaqtga asoslangan fluoressensiya yashash vaqti o‘lchanganda 9 ns ga tengligini ko‘rsatdi (7-rasm).

Bu esa ayni polosa triplet holat emas, balki singlet holatda sodir bo‘lishini tasdiqlaydi. Ligand strukturasida qo‘shimcha yon zanjirlarning bo‘lmasligi shunday qisqa fluoressensiya yashash davriga ega bo‘lishiga sabab bo‘ladi. Fenantrolin molekulasiga 4 ta metil guruhining biriktirilishi temir bilan hosil qilingan kompleks birikmaning nisbatan qattiq (bukilmaydigan) bo‘lishiga sabab bo‘ladi va nurlanish bilan amalga oshadigan yangi deaktivatsiya yo‘llarini ochishi mumkin. Buning natijasida 825 nm atrofida joylashgan kuchsiz emission polosa metalldan ligandga zaryad ko‘chishi (metal to ligand charge transfer – MLCT) o‘tishlardan kelib chiqishi mumkin (6-rasm ichidagi spektr). Bu fikr 825 nm dagi emission polosaning 540 nm dagi absorbsion spektr bilan ko‘zgudagi aks shaklida bo‘lishi mumkinligi ham tasdiqlaydi, lekin 825 nm dagi emission polosaning tabiatini to‘liq tushunish uchun uning vaqtga bog‘liq fluoresensiya spektrini olish kerak.

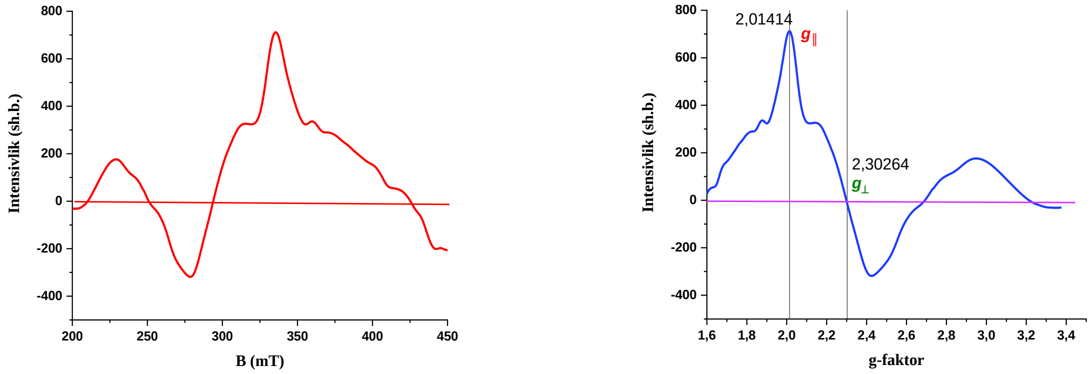
Vaqtga bog‘liq fluoressensiya spektrini olish uchun turli erituvchilar ishtirokida jarayon amalga oshirildi (1-jadval).

1-jadval

$[Fe(tmphen)_3]^{2+}$	n	a_1	a_2	a_3	τ_1	τ_2	τ_3	$\overline{\tau}$	χ_R^2
ACN	3	1,737	3,045	6,686	11,540	1,051	4,49	4,645	1,2200
DMSO	2	1,186	10,399	-	10,620	3,780	-	4,481	1,4040
DMF	2	2,125	9,451	-	9,000	3,277	-	4,327	1,5940
MeOH	2	2,893	8,461	-	8,177	2,538	-	3,975	1,9980

1-jadvaldagi natijalar asosida quyidagi formulalar orqali turli erituvchilarda erigan $[Fe(tmphen)_3]^{2+}$ kompleksning o‘rtacha yashash davri qiymati hisoblandi. Barcha natijalar $\overline{\tau} = \sum_i f_i \tau_i$ yoki $f_i = \frac{a_i \tau_i}{\sum a_i \tau_i}$ formulalar asosida hisoblandi. Atsetonitrildagi o‘rtacha yashash davri boshqa erituvchilarga nisbatan uzoqroq ekanligi aniqlandi.

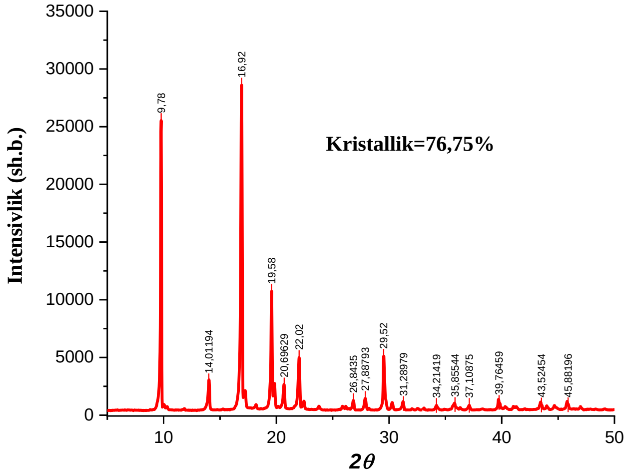
$[Co(tmphen)_3](PF_6)_2$ kompleksning EPR spektrlariga ko‘ra (8-rasm). kompleks hosil qiluvchi Co^{2+} ioni d^7-elektron konfiguratsiyaga ega. Spektrdan ayni kompleks ideal oktaedr bo‘lmasdan, aksial yo‘nalishlarda simmetriyali bo‘lib, z-o‘qi bo‘yicha farq qilishini tasdiqlaydi, ya’ni Yan-Teller effekti kuzatiladi. Bundan kelib chiqib, markaziy ion izotropik maydonda emas, tetragonal ligand maydonida joylashgan deb xulosa qilish mumkin. Ayni kompleksning elektron yutilish spektridagi yuqori molyar ekstinksiya koeffitsiyentiga egaligi ham ushbu fikrni tasdiqlaydi (ya’ni, kompleks sentrosimmetrik emas).



8-rasm. $[Co(tmphen)_3](PF_6)_2$ kompleksning EPR spektri

g faktorning 2,01414 va 2,30264 kabi farqlari kompleksning anizotropik maydon tuzilishi va orbital momentlar ta’siridan kelib chiqadi. Bu farqlar elektroning spin momenti va orbital momentlarining o‘zaro ta’siri hamda tetragonal simmetriya yoki assimmetriya tufayli paydo bo‘ladi. EPR spektrdagi bu farqlar energetik darajalar va magnit maydonlar ta’sirini ko‘rsatib, g faktorning o‘zgarishiga olib keladi.

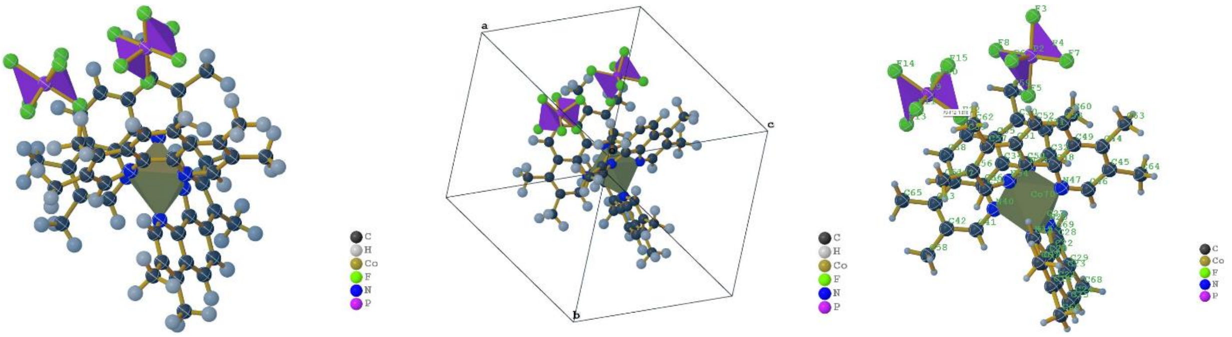
$[Co(tmphen)_3](PF_6)_2$ ning difraktogrammasida mos Breg burchaklarida cho‘qqilar paydo bo‘ladi, bu esa kompleksning kristall strukturasini va o‘lchamlarini aniqlash imkonini beradi. Difraktogrammadan cho‘qqilar komplekning kristall fazalarini va kiristallik darajasini aniqlandi. $[Co(tmphen)_3](PF_6)_2$ ning difraktogrammasida Co(II) kompleks strukturasiga xos bo‘lgan asosiy cho‘qqilarni 9-rasmda ko‘rish mumkin:



Parametrlar	$[Co(tmphen)_3](PF_6)_2$
a, Å	13,215
b, Å	17,823
c, Å	19,823
α, ^{0}	90^o
β, ^{0}	$96,8^o$
γ, ^{0}	90^o
V, Å3	4636,1
F. G.	P21/n
Singoniya	Monoklin

9-rasm. $[Co(tmphen)_3](PF_6)_2$ kompleksining difraktogrammasi

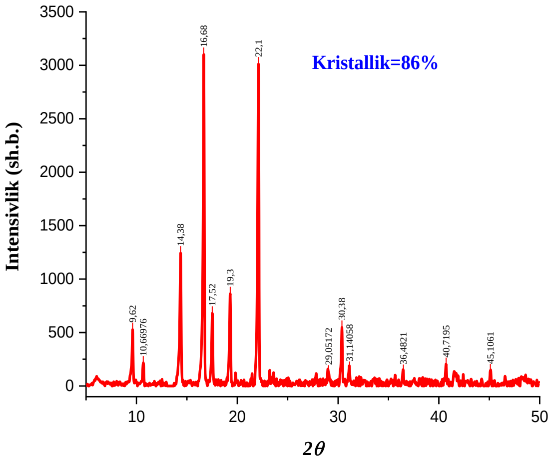
9-rasmda o‘lchashlar xona haroratida va difraksiya burchagi (2θ) 5° dan 50° gacha qadamli rejimda skanerlandi.



10-rasm. [Co(tmphen)$_3$](PF$_6$)$_2$ kompleksning *a,b,c* o‘qlar bo‘ylab kristall tuzilishining ko‘rinishi

9,10-rasmlarda [Co(tmphen)$_3$](PF$_6$)$_2$ tarkibli kompleksning kristall tuzilishi monoklinik holatda bo‘lib, fazoviy guruh: P21/n. Panjara birliklari *a*=13,215 Å, *b*=17,823 Å, *c*=19,823 Å teng bo‘lib, zichligi ρ=1,678 g/cm^3 ga teng. Burchaklari *α*=*γ*=90º, *β*=96,8º. Shuningdek, [Co(tmphen)$_3$](PF$_6$)$_2$ kompleksning kristallik darajasi hisoblanganda 76,75% kristall va 23,25 % amorf tuzilishga ega ekanligi aniqlandi.

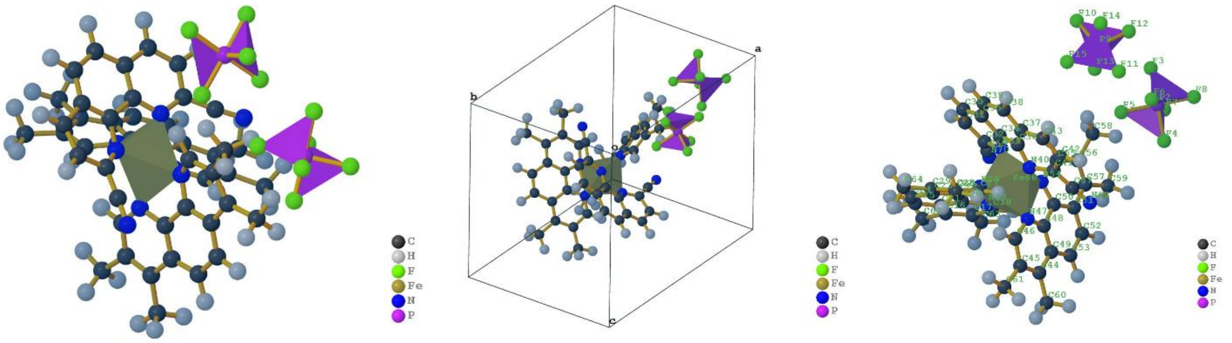
[Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ tarkibli kompleksning kristall tuzilishi triklinik bo‘lib, fazoviy guruhi P1. Panjara birliklari *a* =11,8123 Å, *b*=13,0356 Å, *c*=17,575 Å teng bo‘lib, zichligi ρ=1,662 g/cm^3 ga teng. Burchaklari *α*=91,461º, *β*=101,347º hamda *γ*=99,830 (12-rasm).



Parametrlar	[Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$
a, Å	11,8123
b, Å	13,0356
c, Å	17,575
α, ^{0}	91,461
β, ^{0}	101,347
γ, ^{0}	99,830
V, Å3	2609,5
F. G.	P1
Singoniya	Triklin

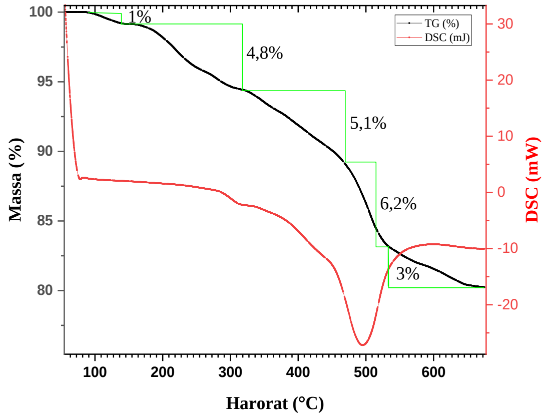
11-rasm. [Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ kompleksining difraktogrammasi

Rentgen difiraksiyasi tadqiqotlari [Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ kompleksning 86% kristall va 14% amorf tuzilishga ega ekanligi ko‘rsatdi. Ayni kompleksning kristallik darajasi yuqoriligi taklif qilinayotgan sintez usuli bu kabi komplekslar olish uchun mos kelishini tasdiqlaydi (11-rasm).

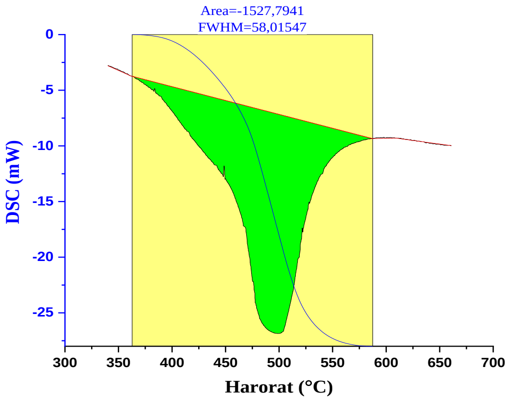


12-rasm. [Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ kompleksning *a,b,c* o‘qlar bo‘ylab kristall tuzilishining ko‘rinishi

Kompleks birikmalarning xossalarini termik usulda aniqlash ular tarkibidagi ligandlar tabiati, soni, shuningdek kompleks birikmaning termik barqaroligi kabi muhim ma’lumotlarlarni beradi. Tahlillar termogravimetrik analiz (TGA) va differensial skanerlovchi kalorimetriya (DSC) birgalikda amalga oshirildi. $[Fe(tmpen)_2(dcbyp)](PF_6)_2$ kompleksining termik tadqiqoti 55 °C dan 675 °C gacha bo‘lgan harorat oralig‘ida o‘tkazildi (13-rasm).



13-rasm. $[Fe(tmpen)_2(dcbyp)](PF_6)_2$ kompleksning derivatogrammasi



14-rasm. $[Fe(tmpen)_2(dcbyp)](PF_6)_2$ kompleksning termik effekti orqali entalpiyasini hisoblash

Kompleks birikmaning termogrammasining DSC chiziqlarida 420-580 °C larda endotermik jarayon kuzatilgan, bu kompleks birikmaning parchalanish harorati 500 °C ga to‘g‘ri keladi. Kompleks $[Fe(tmpen)_2(dcbyp)](PF_6)_2 \cdot nH_2O$ deyarli 100 °C da suvsizlanib, $[Fe(tmpen)_2(dcbyp)](PF_6)_2$ kompleksga aylanadi. 135-315 °C harorat oralig‘ida 6,6 – disiano-2,2-bipiridin(dcbyp) ajralib, massa kamayishi 4,8% ni tashkil etadi. 320-470 °C harorat oralig‘ida 1 mol 3,4,7,8-tetrametil-1,10-fenantrolinning ajralib, massa kamayishi 5,1% ni tashkil etadi. Keyingi massa kamayishi 475-515 °C haroratda amalga oshib, egri chiziqda burilish kuzatildi. Bu esa 3,4,7,8-tetremetil-1,10-fenantrolinning ikkinchi molini yo‘qolishiga mos keladi va massa yo‘qolishi 6,2% ni tashkil etadi. TGA egri chizig‘ida 520-675 °C oralig‘ida massa yo‘qolishi 3% ni tashqil qilib, geksaftorofosfat molekulasi tarkibidan bir molekula ftor chiqib ketishiga va tetraftorofosfat anioni qolishiga mos keladi. Termolizning oxirgi mahsuloti PF_5^- anioniva FeO tashkil qiladi. DSC natijalaridan foydalanib ayni jarayon uchun entalpiya o‘zgarishi 353 kJ/mol teng bo‘ldi (14-rasm).

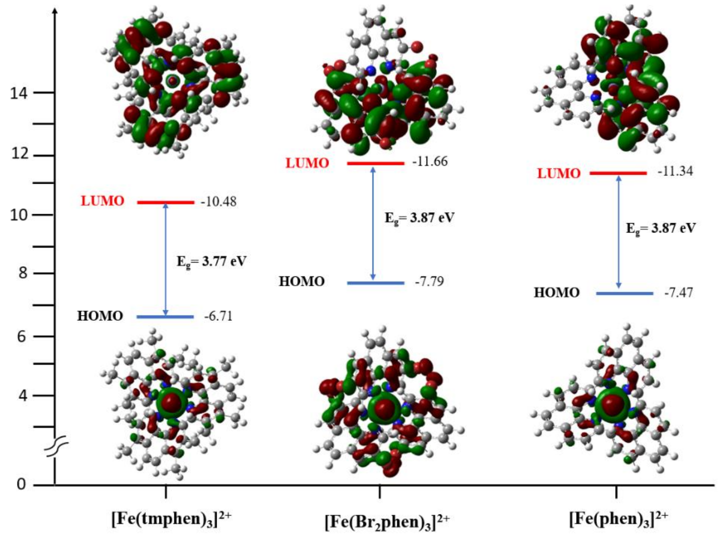
Sintez qilingan komplekslar tuzilishini kvant kimyoviy baholash. Komplekslarning tuzilishi kvantokimyoviy tahlil qilindi va bir qancha tanlangan orbitalar haqida ma’lumotlar 2-jadvalda keltirildi. HOMO va HOMO ga yaqin orbitalar (HOMOlar) asosan markaziy temirning d-orbitalaridan tashkil topgan. LUMO lar to‘plami esa asosan ligandlardan iborat. HOMO va LUMO orbitalarining shakli 15-rasmda ko‘rsatilgan bo‘lib, HOMO orbitalarining degeneratsiyalangan va asosan metallning d_{z^2} va $d_{x^2-y^2}$ orbitalaridan tashkil topganligi ko‘rinadi. LUMO esa ligandlarning p-orbitalaridan tashkil topgan. 3-jadvalda temirning 3 xil ligandlar bilan hosil qilgan komplekslarining HOMO va LUMO orbitalari taqqoslash uchun foydalanildi.

2-jadval.

Brikma	HOMO (eV)	LUMO (eV)	E_g (eV)
$[Fe(phen)_3]^{2+}$	-11,34	-7,469	3,87
$[Fe(Br_2phen)_3]^{2+}$	-11,66	-7,795	3,87
$[Fe(tmphen)_3]^{2+}$	-10,48	-6,710	3,77
$[Co(phen)_3]^{2+}$	-10,87	-7,514	3,36
$[Co(tmphen)_3]^{2+}$	-11,28	-7,844	3,44
$[Ni(phen)_3]^{2+}$	-10,94	-7,630	3,31
$[Ni(Br_2phen)_3]^{2+}$	-11,34	-7,967	3,37
$[Ni(tmphen)_3]^{2+}$	-10,13	-6,757	3,37

3-jadval.

	$Fe(phen)_3]^{2+}$	$Fe(Br_2phen)_3]^{2+}$	$Fe(tmphen)_3]^{2+}$
HOMO			
M	77,83	41,72	72,40
L1	7,30	18,50	9,48
L2	6,95	19,41	9,26
L3	7,92	20,37	8,86
LUMO			
M	9,36	12,88	10,45
L1	30,25	3,33	46,12
L2	26,98	43,19	2,70
L3	33,41	40,60	40,73



15-rasm. Turli temir asosli kompleksalarda HOMO va LUMO energiylari farqi. Markaziy ion temir bo‘lgan komplekslarini HOMO va LUMO tarkibini solishtirish. (L –ligandlar, M – Fe)

$Fe(Br_2phen)_3]^{2+}$, kompleksida HOMO orbitalari ko‘p qismi ligandlarda joylashib, metallning ulushi 41,72 % ni tashkil qiladi. Bu esa qolgan ikki kompleksidan sezilarli farq qiladi. Chunki, uning HOMO orbitalari asosan sof metall orbitalaridan (72,4%) iborat. Kompleksining qo‘zg‘algan holatidagi HOMO va LUMO orbitalarining tarkibi o‘zining asosiy holatidagi kompleksidan farq qilishi aniqlandi.

Dissertatsiyaning “**Fe(II) gomoleptik va geteroleptik komplekslarining fotosensibilizatorlarda qo‘llanilishi**” deb nomlangan **to‘rtinchi bobida** komplekslarning fotosensibilizatorlik xossalarini tadqiq qilish bo‘yicha olingan amaliy va nazariy ma’lumotlarning tahlili keltirilgan.

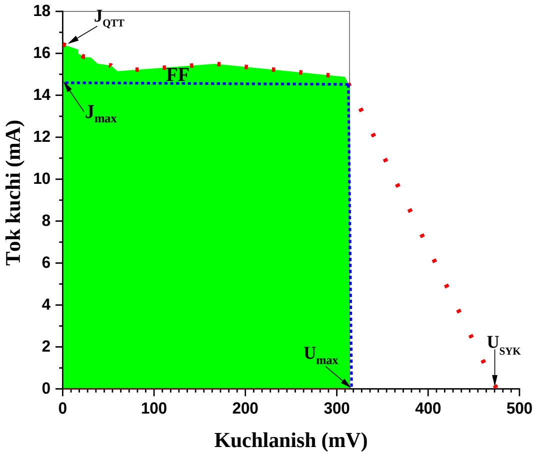
$[Fe(tmphen)_3](PF_6)_2$ gomoleptik kompleksining fotosensibilizatorlik xususi–yatlari o‘rganilgan. Salt yuruvchi kuchlanish (potensial) (U_{SYK}) - tashqi zanjirda tok o‘tmaganda nurlanish ostida yacheyka tomonidan ishlab chiqilgan potentsial hisoblanadi. Uning maksimal termodinamik qiymati yorug‘lik ostidagi ZnO mate–rialning Fermi darajasi va oksidlanish-qaytarilish mediatorining Nernst potensiali–dan farqi bilan aniqlanib, unga fazalararo zaryadning rekombinatsiya tezligi kuchli ta’sir qiladi – maksimal quvvatga to‘g‘ri keluvchi fototok (J_{max}) - nol potensial qo‘llanilganda, yorug‘lik ostidagi 0 potensialdagi tok oqim zichligi aniqlandi. Bo‘yoqlarga sezgir bo‘lgan quyosh elementlarining har tomonlama ishlashini baholash odatda ikkita asosiy kattalikdan ifodalanadi. Birinchisi bu fill faktor va foydali ish koeffitsienti hisoblandi. Quyida (1) va (2) tenglamalarda ifodalangan fill faktor (FF) va foydali ish koeffitsiyenti (η) hisoblash mumkin (16-rasm).

$$FF = \frac{U_{max} \cdot J_{max}}{U_{SYK} \cdot J_{QTT}} \qquad (1) \qquad \eta = \frac{U_{SYK} \cdot J_{QTT} \cdot FF}{P_U} . 100 \qquad (2)$$

BSQE tok kuchi va kuchlanish bog‘liqligi 4-jadvalda o‘lchash natijalari keltirilgan.

4-jadval.

№	Qarshilik R (Om)	Tok kuchi J (mA)	Kuchlanish U(mV)	Quvvat $P_{max}=J_{max}\cdot U_{max}$
1	0	16,43	16	262,88
2	0,5	16,18	17	275,06
3	1	15,98	17	271,66
4	3	15,92	20	318,4
5	5	15,83	23	364,09
6	10	15,80	31	489,80
7	15	15,51	38	589,38
8	25	15,42	53	817,26
9	50	15,15	60	909,00
10	100	15,05	167	2513,35
11	200	14,88	309	4597,92
12	∞	0,00	465	0,00



16-rasm. *J-U* bog‘liqlik grafigi

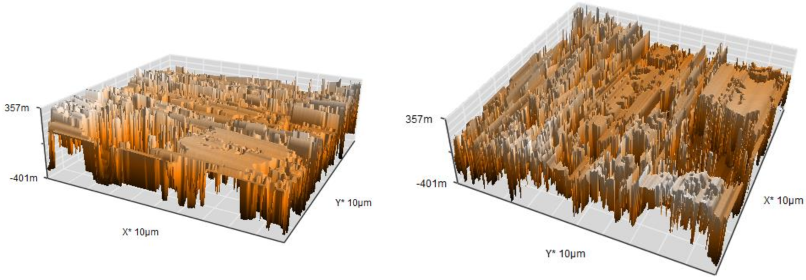
4-jadvaldan quydagi kataliklar aniqlandi:
U_{SYK} – 465 mV yoki 0,465 V
U_{max} – 309 mV yoki 0,309 V
J_{QTT} – 16,43 mA
J_{max} – 14,88 mA
P_u – nurlanishning umumiy quvvati
FF = 0,602 (1-tenglamadan)
η= 5,72% (2-tenglamadan)

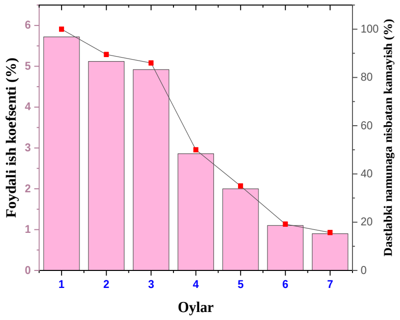
Ushbu tadqiqot davomida AM1.5G simulyatoridan foydalanilganligi uchun konversiya unumi 5,72% ni tashkil qilldi. Agar tabbiy quyosh nurlaridan foydalanilganda kuchlanish 0,94 V gacha yetishi kuzatildi.

$[Fe(tmphen)_2(dcbyp)](PF_6)_2$ geteroleptik kompleksning solishtirma qarshilik, kuchlanish va tok kuchi qiymatlari o‘lchanganda: J_{QTT} – 16,95 mA; J_{max} – 14,95 mA; U_{SYK} – 485 mV; U_{max} – 330 mV; FF = 0,60 teng bo‘lishi qayd qilindi. AM1.5G simulyatoridan foydalanilganligi uchun konversiya unumi 6,14 % ni tashkil qilldi. Tabiiy quyosh nurlaridan foydalanilganda kuchlanish esa 1,03 V gacha yetishi kuzatildi.

Ma’lumki, BSQE larida fotoanod sifatida eng ko‘p ishlatiladigan material bu mezog‘ovak TiO_2 hisoblanadi. Fotoanod sifatida qo‘llash uchun ta’qiqlangan zona energiyasi katta bo‘lgan yarimo‘tkazgich mos keladi. Sensibilizatorning fotoanodga yaxshi immobillashishi yakuniy mahsulotning ishlashiga ijobiy ta’sir qiladi. Tadqiqotlarimizda ZnO fotoanod materiali ishlatildi va uning o‘tkazuvchan zona va zona chegarasi energiyasi anataznikiga mos keladi, lekin ZnO da elektron harakati TiO_2 nikiga qaraganda tezroq. ZnO kimyoviy jihatdan TiO_2 ga qaraganda kimyoviy faolligi uchun kuchli ishqoriy va kislotali muhitlarda tez ishdan chiqadi.

Tadqiqotlarda ZnO qatlamini 96% li etanolda suspenziyasi hosil qilinib, keyin FTO shishaga yotqizilgan edi. Tayyorlangan qatlam ustiga BSQE immobilizatsiya qilib, quritilgandan keyin, ular morfologiyasini nanometr masshtabda o‘rganish uchun atom kuchi mikroskopidan foydalanildi (17-rasm).





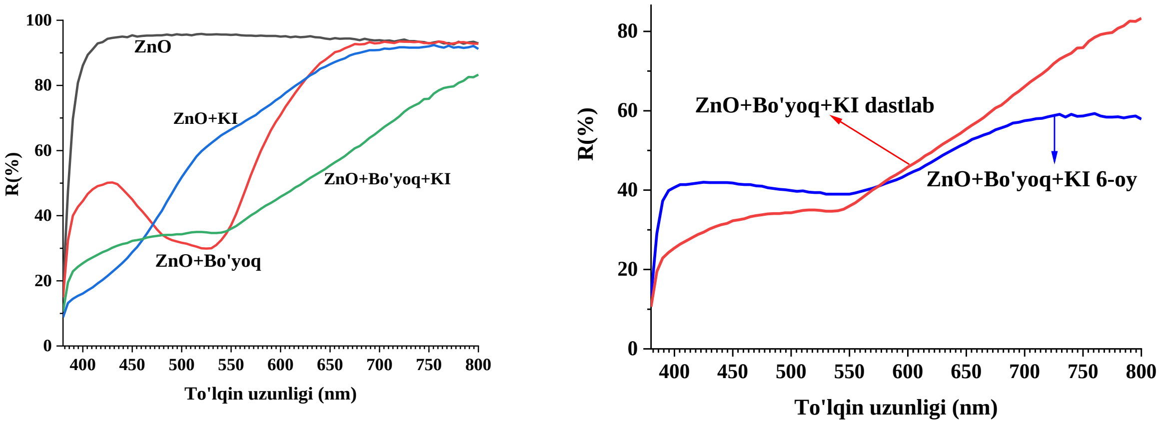
17-rasm. BSQE yuza morfologiyasi AKM yordamida olingan tasviri

18-rasm. Tayyorlangan BSQE ishlash barqarorligi

17-rasmdan koʻrinib turibdiki AKM da olingan tasvirlar yuzasi 10 µm × 10 µm boʻlganda, namuna sirtidagi gʻadir-budirliklarning oʻlchovi eng yuqori choʻqqisi 357 nm boʻlsa, eng past chuqurlik 401 nm ni tashkil qilgan. Natijalar ZnO BSQE uchun mezogʻovak fotoanod vazifasini bajarish uchun mos kelishini koʻrish mumkin.

Natijalar tayyorlangan BSQE 3 oy davomida barqaror ishlashinini, keyin foydali ish koeffitsiyenti 3% dan pastga tushib ketganini koʻrish mumkin (18-rasmda). Buning sababi quyidagilar: ZnO tashqi muhit ta’sirida kimyoviy oʻzgarishga uchrashi va adsorbsion qobiliyati pasayishi; sensibilizator molekulasining vaqt oʻtishi bilan parchalanishi; mediator konsentratsiyasining kamayishi hisobiga BSQE ishlash unumi pasayishi.

19a-rasmda fotoanod sifatida ishlatilgan ZnO qatlamining, unga sensibilizator yotqizilgandagi, shuningdek KI va boʻyoq bilan birgalikdagi diffuz aks etish spektri keltirilgan. Spektrdan ZnO 430 nm dan 800 nm gacha keng sohada koʻrinadigan nurlarni yutmasligi, shuning uchun fotoanod materiali sifatida mos kelishini koʻrish mumkin. Mediator sifatida KI qoʻshilganda, sensibilizator qoʻshilganda, shuningdek mediator va boʻyoq qoʻshilganda barcha moddalar oʻz fotokimyoviy xossasini saqlab qolishi kuzatildi. Bu esa BSQE da yarimoʻtkazgich ZnO materialariga barcha moddalar fizik adsorbsiyalanganligini tasdiqlaydi.



a) **b)**

19-rasm. a) ZnO, KI@ZnO, boʻyoq@ZnO, KI+Boʻyoq@ZnO diffuz aks etish spektri; b) yangi tayyorlangan va 6 oydan keyingi KI+boʻyoq@ZnO diffuz aks etish spektri

19b-rasmda esa tayyorlangan materialning 6 oydan keyingi diffuz aks etish spektri keltirilgan. Spektrdan BSQE barqarorligi kamayishiga asosan sensibilizator (boʻyoq) va mediator sabab boʻlishini koʻrish mumkin.

XULOSALAR

1. Fe(II), Co(II), Ni(II) ionlarining organik ligandlar (6,6 – disiano-2,2-bipiridin, 3,8-dibromo-1,10-fenantrolin, 2,2-bixinolin, 3,4,7,8-tetrametil-1,10-fenantrolin) hamda suv va spirt molekulalari ishtirokida 32 ta yangi gomoleptik va geteroleptik komplekslari sintez qilindi. Ularning tarkibi, tuzilishi, organik ligandlardagi N (azot) donor atomlari orqali koordinatsiyalanishi, markaziy atomlarning elektron konfiguratsiyasi o‘zgargan oktaedrdan iborat ekanligi EPR, elektron yutilish, IQ, Raman spektrlari yordamida aniqlandi.

2. Gaussian 16W dasturi DFT usuli bilan kvant-kimyoviy hisoblashlar orqali ligandlarning elektron, geometrik tuzilishlari, energetik parametrlari va nazariy koordinatsion markazlarining ehtimolligi topildi hamda komplekslarda HOMO va LUMO energiyalar farqiga asoslanib yarimo‘tkazgich xossalari aniqlandi.

3. Sintez qilingan komplekslarda lyuminessensiya yashash davrini boshqa erituvchilarga nisbatan asetonitrilda uzoqroq, ya’ni $[Fe(tmphen)_3]^{2+}$ $\tau=9$ ns, $[Fe(tmphen)_2(dcbyp)]^{2+}$ $\tau=10$ ns ekanligi pico Quant spektro fluorometrda o‘lchandi. Emmission polasa metalldan ligandga zaryad ko‘chishidan kelib chiqishi aniqlandi (MLCT). $[Co(tmphen)_3](PF_6)_2$ kompleksning EPR spektr tahliliga ko‘ra ideal oktaedr bo‘lmasdan, aksial yo‘nalishlarda simmetriyali bo‘lib, z-o‘qi bo‘yicha farq qilib, Yan-Teller effekti kuzatiladi. Difraktogramma tahliliga ko‘ra kristall tuzilishi monoklinik ekanligi aniqlandi.

4. Sintez qilingan kompleks birikmalarning termik va eritma holatdagi barqarorlik konstantalari ligandlar tabiatiga bog‘liqligi hamda Fe(II) komplekslarining barqarorlik konstantalari hisoblanib, ularning qiymatlari bo‘yicha $[Fe(tmphen)_3]^{2+}$ gomoligandli kompleksi eng barqaror ekanligi aniqlandi. Turli gomoligandli komplekslar $K_{beqaror}$ qiymati ular tarkibidagi yonaki radikalning tarkibi va tuzilishiga bog‘liqligi izohlandi. Termogrammalardagi endo-va ekzoeffektlarning hosil bo‘lish sabablari aniqlanib, termik desturksiya mahsulotlari identifikatsiyalandi, shuningdek, komplekslarning termik parchalanishi bosqichma-bosqich borishi va ayni jarayonlar uchun entalpiya qiymatlari hisoblandi.

5. Sintez qilingan temir (II) gomo- va geteroligandli komplekslarning elektron yutilish va voltamper tahlil ma’lumotlariga asoslanib, quyosh elementlari tayyorlashda quyosh nuriga sezgir bo‘yoq modda sifatida foydalanish imkoniyati aniqlandi. AM1.5 simulyatoridan foydalanilganda konversiya unumi 5,72% dan 6,14% gacha, quyosh nurlaridan foydalanilganda 11% dan 12% gacha yetishi kuzatildi.

6. Fe(II), Co(II), Ni(II) ionlarining gomo- va geteroligandli kompleks birikmalari Rossiya Federatsiyasining “FLUID” MChJ, “Elektrokimyozavod” qo‘shma korxonasi aksiyadorlik jamiyati qoshidagi “ELKIMYO – AGROHIMOYA” MChJ hamda “BMAX BUILDING MATERIALS” MChJda sinovdan o‘tkazildi va BSQE olish uchun qo‘llashga tavsiya berildi.

SCIENTIFIC COUNCIL DSc. 03/30.12.2019.K.01.03 FOR THE AWARD OF ACADEMIC DEGREES AT NATIONAL UNIVERSITY OF UZBEKISTAN
SAMARKAND STATE UNIVERSITY NAMED AFTER SHAROF RASHIDOV

TOSHPULATOV DOSTON TOLMAS UGLI

SYNTHESIS AND PHOTOCHEMICAL STUDY OF HOMOLEPTIC AND HETEROLEPTIC COORDINATION COMPOUNDS OF SOME 3d METALS

02.00.01 – Inorganic chemistry

DOCTOR OF PHILOSOPHY IN CHEMISTRY (PhD)
ABSTRACT OF THE DISSERTATION

Tashkent – 2025

The theme of the Doctor of Philosophy (PhD) dissertation in chemical sciences is registered in the Higher Attestation Commission under the Ministry of Higher Education, Science and Innovation of the Republic of Uzbekistan under the number B2021.1.PhD/K380.

The dissertation was carried out at National University of Uzbekistan.

The abstract of the dissertation was posted in three (Uzbek, Russian, English (resume)) languages on the website of the Scientific Council at www.ispm.uz and on the website of "ZiyoNet" Information and Educational Portal at www.ziyonet.uz.

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	Razzokova Surayyo Doctor of Philosophy in Chemical Sciences, Docent
Leading organization:	**Institute of general and inorganic chemistry**

The dissertation will be defended on "17" april 2025 at 2.pm hours at the meeting of the Scientific Council No. DSc. 03/30.12.2019.K.01.03 at the at the National University of Uzbekistan (Address: 100174, Tashkent, University street, 4th house). Tel.: (99871) 227-12-24, fax: (99824) 246-02-24, e-mail: ilmiy_kengash@nuu.uz).

The dissertation can be viewed at the Information Resource Center of the National University of Uzbekistan (registered with the number 47). Address: (100174, Tashkent, University street, 4th building, phone: (+99871) 246-67-71.

The abstract of the dissertation was sent out "04" april 2025
(distribution protocol № 12 dated "03" aprile 2025)

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INTRODUCTION (abstract of PhD dissertation)

The relevance and importance of the dissertation title. Due to the increasing demand for energy sources in the world, the synthesis of materials for highly efficient and stable solar cells is of great importance today. Such sensitizers are divided into ultra-pure silicon, inorganic complex compounds, and organic compounds according to their origin. The use of inorganic complex compounds as sensitizers is considered to be more versatile than the other two alternatives. In addition, special attention is paid to the development of environmentally friendly metal complex-type sensitizers that are economically viable, avoiding toxic and high-concentration compounds. In particular, the use of photosensitizers that form a strong protective layer on the metal surface and are effective at low concentrations and in various temperature ranges is important.

The synthesis of complex compounds and their application in various fields has always been one of the most important directions in the world. Ruthenium bipyridine complexes are often used as such inorganic sensitizers, but ruthenium compounds are not only expensive but also toxic. Therefore, the synthesis of cheaper and less toxic metal complex compounds and their use in sensitizers is of great importance.

In our republic, special attention is paid to the development of advanced innovative technologies, as well as the accelerated development of industry. Within the framework of the work carried out in this regard, certain results are being achieved and large-scale activities are being implemented in this area. The Decree of the President of the Republic of Uzbekistan No. PF-60 dated January 28, 2022 “On the Development Strategy of New Uzbekistan for 2022-2026” sets out important tasks aimed at “Further developing the export potential of local industries, fully utilizing existing opportunities.” In this regard, the use of complex compounds of Fe(II), Co(II), and Ni(II) ions in the presence of organic ligands, such as 6,6-dicyano-2,2-bipyridine, 3,8-dibromo-1,10-phenanthroline, 2,2-bixinoline, and 3,4,7,8-tetramethyl-1,10-phenanthroline, as dye-sensitized solar cells is of great importance.

The results of this dissertation research will serve to a certain extent in the implementation of the tasks set out in the Decree[1] of the President of the Republic of Uzbekistan No. PF-60 dated January 28, 2022 “On the Development Strategy of New Uzbekistan for 2022-2026”, No. PQ-3983 dated October 25, 2018 “On measures for the accelerated development of the chemical industry in the Republic of Uzbekistan”, No. PQ-4265 dated April 3, 2019 “On measures to further reform the chemical industry and increase its investment attractiveness”, No. PQ-4992 dated February 13, 2021 “On measures to further reform and financial soundness of chemical industry enterprises, and develop the production of high-value-added chemical products”, and other regulatory legal documents related to this activity.

The conformity of research with priority directions of development of science and technologies of the Republic. This work is related to the development of science and technology of the Republic, specifically under the VII

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[1] Decree of the President of the Republic of Uzbekistan No. PF-60 dated January 28, 2022 :On the Development Strategy of New Uzbekistan for 2022-2026”.

plan. It is being carried out in accordance with the priorities of “Chemical Technology and Nanotechnology”.

The degree of study of the problem. Many scientific researches conducted by scientists all over the world, sensitizers based on inorganic complex compounds are new directions in our Republic and are considered one of the fastest developing directions of research abroad. In this field, professors M.Gratzel and B.Oregan of the University of Berkeley (USA), professor W.Campbell of Massey University (New Zealand), professor M. Stein of the University of Michigan (USA), professor M. Sliwa of the University of Lille (France) and others are dedicated to scientific research.

Currently, a large amount of theoretical and practical data has been accumulated on the use of synthesized complex compounds as dye-sensitized solar cells. In this regard, the research of scientists such as G.Boschloo, I.Benesperi, J. Xavier, L.Gibson, M.Pavone, H.Pettersson, A.Hagfeldt, M.Freitag deserves special attention.

In our country, N.A.Parpiyev, B.T.Ibragimov, T.A.Azizov, X.T.Sharipov, A.A.Shabilolov, X.X.Turayev, B.B.Umarov, Sh.A.Kadirova, J.M.Ashurov, A.B.Ibragimov, Sh.Sh.Daminova and their group have made a great contribution to the synthesis, structure, properties and research of complex compounds. At the same time, an analysis of the literature shows that, despite the extensive experimental results on the analysis of complexes formed by 3d metal salts with organic ligands, the use of complex compounds formed by Fe(II), Co(II), Ni(II) ions in the presence of organic ligands as dye-sensitive solar elements has not been sufficiently studied. Therefore, the synthesis of complex compounds formed by the Fe(II) ion with 3,4,7,8-tetramethyl-1,10-phenanthroline, 6,6-dicyano-2,2-bipyridine ligands, the study of their physicochemical properties, and their use as sensitizers are of particular scientific interest.

The connection of investigation with plans of science-investigated works of the science-investigate institution where dissertation was carried out. Dissertation research is carried out following the scientific direction of the Samarkand State Department of Inorganic Chemistry and Materials Science named after Sharof Rashidov.

The purpose of the study is to synthesize homoleptic and heteroleptic complex compounds of Fe(II), Co(II), and Ni(II) ions in the presence of organic ligands and to study the photochemical properties of the resulting compounds.

The tasks of the research work are:

determination of optimal conditions for the synthesis of homoleptic and heteroleptic complex compounds of Fe(II), Co(II), Ni(II) ions with organic ligands;

determination of the electronic structure, energetic and geometric parameters, and reactivity of complexes of 3d-metals with phenanthroline and bipyridine derivatives using modern quantum-chemical methods;

study of the structure and properties of synthesized homoleptic and heteroleptic complex compounds using modern physicochemical methods;

determination of thermodynamic and solution stability constants of synthesized complex compounds;

study of the use of the obtained complex compounds as dye-sensitized solar cells and as photosensitizers.

The objects of the research work 2,2-bipyridine and 1,10-phenanthroline derivatives, their complexes with Fe(II), Co(II), Ni(II) salts, ZnO, and FTO glasses.

The subject of investigation the study of the composition, structure, individuality, physicochemical, and photosensitizing properties of homoleptic and heteroleptic complex compounds.

The methods of research. Modern research methods such as infrared spectroscopy (IR), UV-visible spectroscopy (UV-vis), diffuse reflectance spectroscopy, Raman spectroscopy, powder X-ray diffraction (XRD), steady state luminescence, time-resolved luminescence, electron paramagnetic resonance (EPR) spectroscopy, differential thermal analysis (DTA), modern quantum-chemical calculations, and determination of resistivity, voltage, and current values were used.

The scientific novelty of the study consists of:

32 new homoleptic and heteroleptic complexes of Fe(II), Co(II), Ni(II) ions in the presence of additional water and alcohol molecules with organic ligands (6,6 – dicyano-2,2-bipyridine, 3,8-dibromo-1,10-phenanthroline, 2,2-bixinoline, 3,4,7,8-tetramethyl- 1,10-phenanthroline) were synthesized;

stability constant values of the homoleptic complexes formed in solution with Fe(II) ions in the presence of 2,2-bipyridine, 6,6 – dicyano-2,2-bipyridine, 3,4,7,8-tetramethyl- 1,10-phenanthroline and their dependence on the nature of the ligands were determined;

using advanced programs of quantum-chemical methods, the geometric and energy parameters of the synthesized complex molecules, the distribution of charges on atoms, and reaction centers were determined;

The thermal properties of the synthesized complexes, the mechanism of thermal decomposition and their quantitative, energetic aspects, as well as the enthalpy change for the same processes were determined using the DSC results.

The electronic transition energy of the synthesized complex was calculated by the Tauc method for both $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ states, based on the suitability of DSSC for sensitizers due to their semiconductor nature;

It was found that the photosensitizing properties of the synthesized complexes with homo- and heteroleptic ligands of Fe(II) ions are 5.72% - 6.14% when using the AM1.5G simulator, and reach 11% – 12% in natural sunlight.

The practical results of the study include:

The optimal conditions for the synthesis of coordination compounds of Fe(II), Co(II), Ni(II) ions in the presence of organic ligands (6,6 – dicyano-2,2-bipyridine, 3,8-dibromo-1,10-phenanthroline, 2,2-bixinoline, 3,4,7,8-tetramethyl-1,10-phenanthroline) were determined;

Based on the analysis of the time-resolved fluorescence spectrum of the synthesized new complexes, it was determined that the fluorescence lifetime in acetonitrile solution is 7-10 ns.

When evaluating the performance of the synthesized new complex compounds as dye-sensitive solar cells, it was found that the fill factor is in the range of 0.6-0.65.

It was found that when complexes of Fe(II), Co(II), Ni(II) ions with 2,2-bipyridine and 1,10-phenanthroline derivatives in solution are used for dye-sensitized solar cells, the useful work coefficient is 5.72 – 6.14%, since the dyes have photosensitizing properties and a high absorption coefficient.

2,2-bipyridine and 1,10-phenanthroline derivatives, their complex compounds with Fe(II), Co(II), Ni(II) ions are recommended as DSSC.

The reliability of obtained results. It is based on modern research methods such as infrared spectroscopy (IR), UV-visible spectroscopy (UV-vis), diffuse reflectance spectroscopy, Raman spectroscopy, powder X-ray diffraction (XRD), steady-state luminescence, time-resolved luminescence, electron paramagnetic resonance (EPR) spectroscopy, differential thermal analysis (DTA), modern quantum-chemical calculations, and determination of resistivity, voltage, and current values.

The scientific and practical value of the results of the research.

The scientific significance of the research results is explained by the monitoring of scientific literature on complexes of Fe(II), Co(II), Ni(II) ions with organic ligands, the study of the composition, structure, donor atom coordination, stability constants, physicochemical analysis methods of newly synthesized complexes, the determination of electrochemical parameters such as photosen–sitizing properties, specific resistance, voltage and current of $[M(N)_3]$ complexes.

The significance of the research results will serve to develop methods for the synthesis and solid-state extraction of new complex compounds, and their use in solar cells based on dye-sensitized solar cells due to their semiconducting and optical properties.

Implementation of the research results. Based on the scientific results obtained on the production of inorganic complex compounds for solar cells:

It was put into practice at “ELKIMYO – AGROHIMOYA” LLC under the joint venture “Elektrokimyozavod” (Reference No. 92 of JSC “Elektrokimyozavod” JV dated May 6, 2024). It formed colored complexes with 2,2-bipyridine and 1,10-phenanthroline derivatives containing Fe^{2+}, Co^{2+}, Ni^{2+} ions, which allowed detecting the presence of target molecules at low concentrations of 3d metal ions up to 0.0025 mol/l. Included in the innovative development program of JSC “Elektrokimyozavod” JV for 2026-2028;

Implemented in the joint venture “BMAX BUILDING MATERIALS” LLC (Reference No. 74/A of “BMAX BUILDING MATERIALS” LLC dated April 5, 2024). It was found that 3 homoleptic and 4 heteroleptic complexes of Fe(II) ion; 5 homoleptic and 8 heteroleptic complexes of Co(II) ion; 5 homoleptic and 7 heteroleptic complexes of Ni(II) ion when used for dye-sensitized solar cells have photosensitizing properties and a high assimilation coefficient of dyes.

Implemented in the joint venture “FLUID” LLC of the Russian Federation (Reference No. 94 of “FLUID” LLC dated April 3, 2024). Homoleptic of 3d-metals $[Fe(L_1)_3](PF_6)_2$, $[Co(L_1)_3](PF_6)_2$, $[Ni(L_1)_3](PF_6)_2$, $[Fe(L_4)_3](PF_6)_2$, $[Co(L_4)_3](PF_6)_2$, $[Ni(L_4)_3](PF_6)_2$; heteroleptic $[Co(L_1)(L_2)_2](PF_6)_2$,

$[Fe(L_4)_2(L_1)](PF_6)_2$, $[Co(L_1)(L_4)_2](PF_6)_2$, $[Ni(L_1)(L_4)_2](PF_6)_2$, $[Ni(L_1)(L_2)_2](PF_6)_2$, $[Ni(L_1)_2(L_4)](PF_6)_2$ complexes were used for dye-sensitized solar cells and the dyes were found to have photosensitizing properties and high absorption coefficients.

Approbation of the research results. The results of this research were presented and discussed at 16 scientific and practical conferences, including 5 international and 11 national.

The publication of results of investigation. A total of 23 scientific works have been published on the topic of the dissertation, of which 7 articles have been published in scientific publications recommended for publication of the main scientific results of Doctor of Philosophy (PhD) dissertations by the Higher Attestation Commission of the Republic of Uzbekistan, including 5 articles in republican and 2 articles in international journals and 5 in international scientific conferences, and 10 theses have been published in republican scientific and practical conferences.

The structure and volume of dissertation. The dissertation consists of an introduction, 4 chapters, a conclusion, A list of used literature and an appendix. The volume of the dissertation is 120 pages.[2]

MAIN CONTENT OF DISSERTATION

In the introduction establishes the relevance and necessity of the research, presents the goals and objectives, describes the object and subject, indicates the correspondence of the research to the priority areas of development of science and technology of the republic, describes the scientific novelty, scientific and practical significance of the research results, reveals the scientific and practical significance, reliability of the results obtained, their application to practice, and provides information on published works and the structure of the dissertation.

The first chapter, entitled **“Types of photosensitizers and prospects for the application of 3d metal complexes in dye-sensitized solar cells,”** summarizes the information in the international and national scientific literature on this topic, and as a result of their analysis, the purpose, objectives, and relevance of the work are established.

The second chapter, entitled **“Synthesis and research methods of complex compounds of 3d (Fe^{2+}, Co^{2+}, Ni^{2+}) metals”,** provides information on modern research methods such as the study of the formation of complex compounds in solution, the synthesis and structure determination of complex compounds, infrared spectroscopy, UV-vis spectroscopy, diffuse reflectance spectroscopy, Raman spectroscopy, powder X-ray diffraction, steady state luminescence, time-resolved luminescence, electron paramagnetic resonance spectroscopy, differential thermal analysis, quantum chemical calculations, and determination of specific resistance, voltage, and current values.

The formation of complexes of 3d metals with organic ligands was studied from several literatures, and optimal conditions for synthesis were selected. Based

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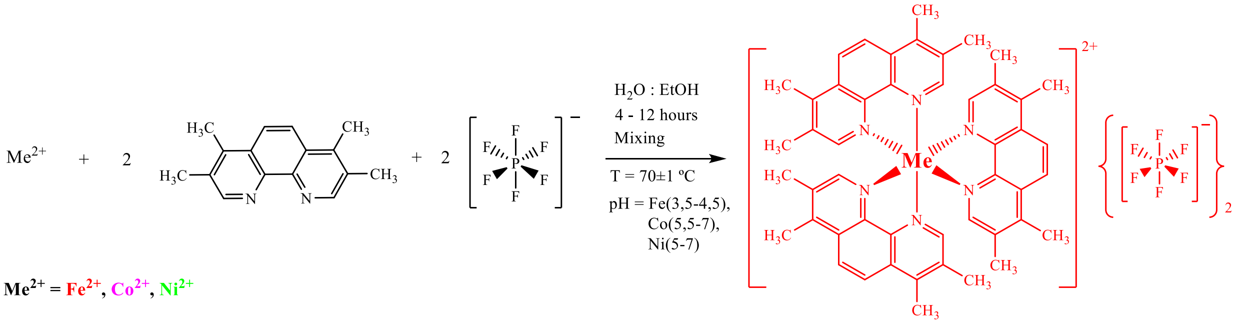
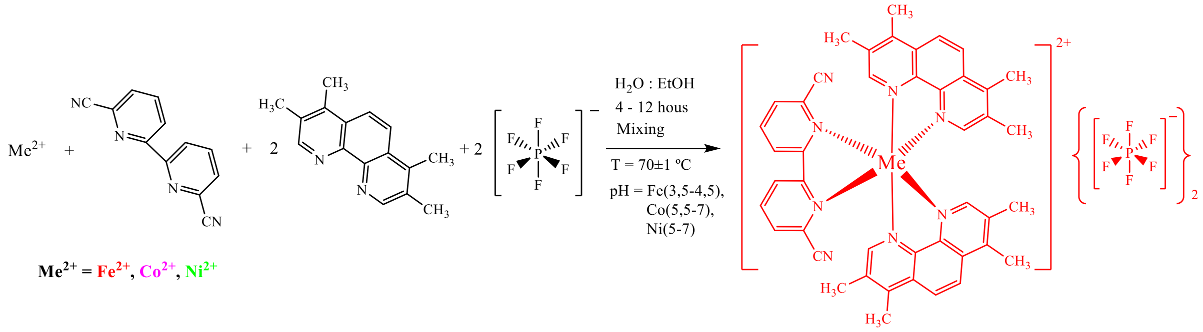
[2] I would like to express my gratitude to PhD, associate professor Kh.Sh. Tashpulatov for his valuable advice during the completion of my thesis.

on the selected conditions, the complex formation of iron, cobalt, and nickel ions with 6,6-dicyano-2,2-bipyridine, 3,8-dibromo-1,10-phenanthroline, 2,2-biquiqino–line, 3,4,7,8-tetramethyl-1,10-phenanthroline ligands, as well as the precipitation process and the process of isolating the substance in pure form were studied from the literature, and a synthesis scheme was proposed with some modifications.



Scheme 1. Preparation of homoleptic complexes



Scheme 2. Preparation of heteroleptic complexes.

To synthesize homo- and hetero-liganded complexes of the main ligands 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) and 6,6–dicyano-2,2-bipyridine (dcbyp) with Fe^{2+}, Co^{2+}, Ni^{2+} ions, Me^{2+}:L=1:3 mol ratio was used, and 2 mol NH_4PF_6 was used as a precipitant. Ammonium hexafluorophosphate was used as a source of weak complex-forming anion PF_6^- in the synthesis of complex compounds, this substance was used in the study due to its inertness and ability to stabilize certain metal complexes. When synthesizing complex compounds in solution, a weakly acidic to neutral environment was required, and complex formation was achieved at temperatures ranging from 60 °C to 80 °C. However, a specific pH and temperature are required for the synthesis of each complex.

The third chapter, entitled **“Physicochemical studies of homoleptic and heteroleptic complexes of 3d (Fe^{2+}, Co^{2+}, Ni^{2+}) metals”,** presents the results of the study of the structure and physicochemical properties of the synthesized complex compounds.

The FTIR spectrum of the synthesized complex and precursors is shown in Figure 1. As can be seen from the spectrum, the functional group region of $[Fe(tmphen)_3](PF_6)_2$ is almost empty (blue line). The first group of absorption bands is located in the range of 1400-1700 cm^{-1} and is attributed to the stretching vibrations of the aromatic ring of the tetramethylphenanthroline ligand.

That is, the C=N stretching vibration band appeared at 1596 cm^{-1} and the C=C stretching vibration band at 1574 cm^{-1}. A narrow sharp band of moderate intensity is visible at 720 cm^{-1} and is related to the stretching vibration of the C–H group. The second group of vibrations is located around 870 cm^{-1} and is related to the stretching vibrations of the hexafluorophosphate anion. The following shifts in the stretching bands indicate that a coordination bond is formed between the nitrogen atom (donor) and the iron(II) ion (acceptor) during complex formation. That is, when the stretching vibration frequency of the C=N bond shifts from 1612 cm^{-1} to 1596 cm^{-1}, the stretching frequency of the phenanthroline aromatic ring C=C shifts from 1565 cm^{-1} to 1574 cm^{-1}.

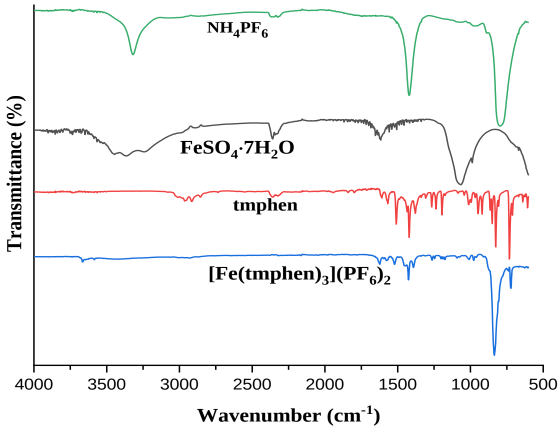


Figure 1. FTIR spectra of [Fe(tmphen)$_3$](PF$_6$)$_2$ complex and precursors.

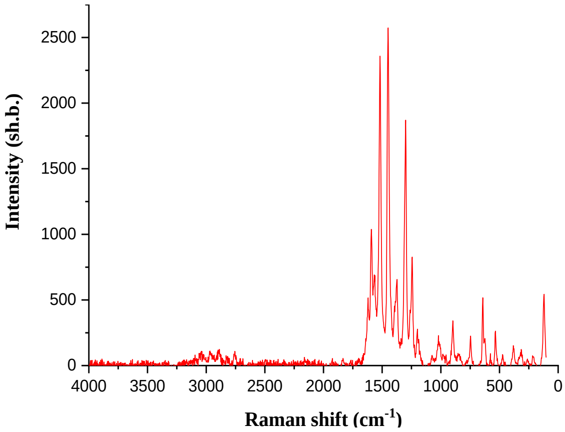


Figure 2. Raman spectrum of [Fe(tmphen)$_3$](PF$_6$)$_2$ complex.

The Raman spectrum of the [Fe(tmphen)$_3$](PF$_6$)$_2$ complex is shown in Figure 2 and is complementary to the IR spectrum shown in Figure 1. The main vibrational bands in this spectrum are located below 2000 cm^{-1}. The main strong and sharp bands in the Raman spectrum of the sample are located at 1511, 1446 and 1300 cm^{-1} and are attributed to the symmetrical stretching vibrations of the phenanthroline aromatic ring. The weak Raman signal at 630 cm^{-1} is attributed to the P–F stretching vibrations of the hexafluorophosphate anion.

The synthesized [Fe(tmphen)$_3$](PF$_6$)$_2$ complex was dissolved in various solvents from non-polar to polar: dimethylsulfoxide, dimethylformamide, tetrahydrofuran, acetone and acetonitrile. In this study, acetonitrile was chosen as the most suitable solvent and the specific photophysical properties of the complex were studied. In the remaining solvents, the complex was unstable or did not exhibit fluorescence properties. This is due to the high rate of radiationless relaxation processes.

The optical properties of the complex depend on their electronic structure and the transitions between them. If an electron transition is allowed by the selection rule, the greater the probability of its occurrence and the correspondingly larger the value of ε. It is known that 3 different selection rules apply to d-metal coordination compounds. These are the Laporte, spin, and pair selection rules, and it is possible to empirically estimate which transitions are allowed or prohibited in a complex based on the value of its molar extinction coefficient.

To be suitable for use as a sensitizer or mediator for DSSC purposes, the molar absorption (extinction) coefficient of the complex should be high. Therefore, solutions of the [Fe(tmphen)$_3$](PF$_6$)$_2$ complex with concentrations ranging from $1 \cdot 10^{-5}$ M to $8 \cdot 10^{-5}$ M were prepared and the absorbance at 500 nm was measured (Figure 3).

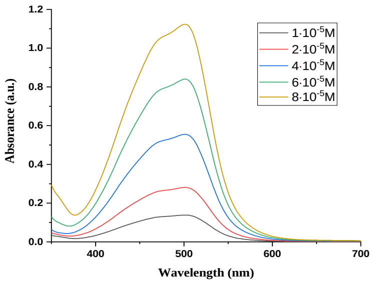


Figure 3. Absorption spectrum of different concentrations of [Fe(tmphen)$_3$](PF$_6$)$_2$ complex in acetonitrile

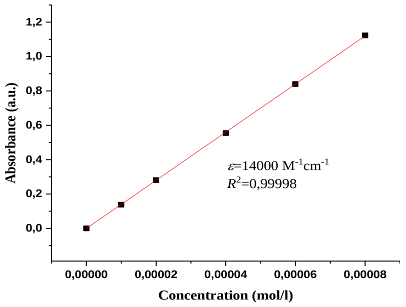


Figure 4. Dependence of absorbance to solution concentrations in acetonitrile of [Fe(tmphen)$_3$](PF$_6$)$_2$ complex

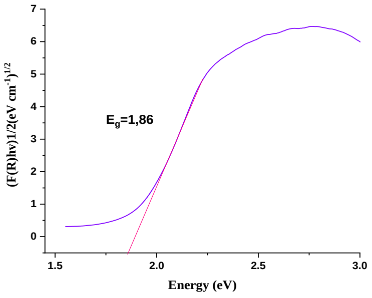


Figure 5. Tauc plot of [Fe(tmphen)$_3$](PF$_6$)$_2$ complex

Using the relationship between the optical density values at 500 nm and the concentration, the molar extinction coefficient of the [Fe(tmphen)$_3$](PF$_6$)$_2$ complex was calculated (Figure 4). From this relationship, it was found that the molar extinction coefficient of the complex is around 14000 $M^{-1}\cdot cm^{-1}$. Such a sufficiently large molar extinction coefficient value indicated that all transitions were allowed in the same complex. To better understand the nature of the bands in the electronic absorption spectrum of the [Fe(tmphen)$_3$](PF$_6$)$_2$ complex, referring to the Tanabe-Sugano diagram, it can be concluded that the band at 500 nm arises from the $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$ transitions.

To assess the semiconducting nature of the [Fe(tmphen)$_3$](PF$_6$)$_2$ complex, the direct and indirect band gap energies (widths) were calculated using the Tauc method (Figure 5). The indirect band gap energy was calculated using the equation $E = (\alpha h\nu)^{1/2}$ and extrapolated to an energy level of 1.86 eV. The calculated semiconducting nature of the complex confirms its suitability as a sensitizer for DSSC.

The absorption and emission spectra of [Fe(tmphen)$_3$]$^{2+}$ in acetonitrile are shown in Figure 6. Its absorption spectrum shows distinct bands at 480, 510, and 540 nm (blue line). It can also be seen that there are additional weak bands at 570 and 590 nm in this spectrum. The emission spectrum of the same complex has a single broad band, with the main band at 440 nm and an emission maximum at 510 nm upon excitation (red line).

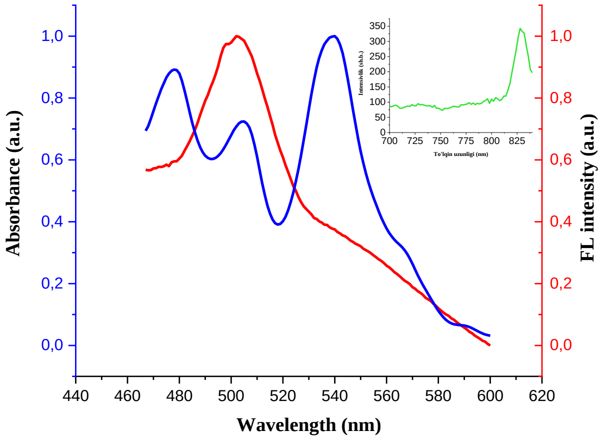


Figure 6. Absorbance spectrum (blue line) and emission spectrum (red line) of [Fe(tmphen)$_3$]$^{2+}$ complex in acetonitrile ; (inset) λ_{exc} = 440 nm.

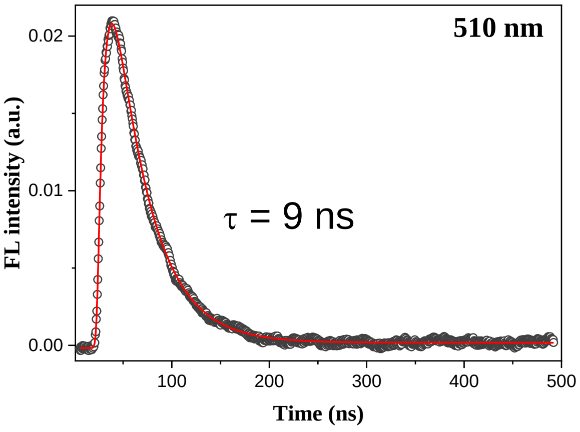


Figure 7. Fluorescence decay curve of [Fe(tmphen)$_3$]$^{2+}$ complex in acetonitrile.

The time-resolved fluorescence spectrum of the compound at 510 nm was measured to be 9 ns (Figure 7).

This confirms that this band occurs in the singlet state, rather than the triplet state. The absence of additional side chains in the ligand structure is responsible for such a short fluorescence lifetime. Attachment of four methyl groups to the phenanthroline molecule makes the complex formed with iron relatively rigid (non-folding) and may open up new deactivation pathways by irradiation. As a result, the weak emission band around 825 nm may arise from metal to ligand charge transfer (MLCT) transitions (spectrum in Figure 3). This also supports the idea that the emission band at 825 nm may be a mirror image of the absorption spectrum at 540 nm, but to fully understand the nature of the emission band at 825 nm, its time-resolved fluorescence spectrum must be obtained.

The process was carried out in the presence of different solvents to obtain the time-resolved fluorescence spectrum (Table 1).

Table 1

$[Fe(tmphen)_3]^{2+}$	n	a_1	a_2	a_3	τ_1	τ_2	τ_3	$\overline{\tau}$	χ_R^2
ACN	3	1.737	3.045	6.686	11.540	1.051	4.490	4.645	1.2200
DMSO	2	1.186	10.399	-	10.620	3.780	-	4,481	1.4040
DMF	2	2.125	9.451	-	9.000	3.277	-	4.327	1.5940
MeOH	2	2.893	8.461	-	8.177	2.538	-	3.975	1.9980

Based on the results in Table 3.1, the average lifetime value of the $[Fe(tmphen)_3]^{2+}$ complex dissolved in various solvents was calculated using the following formulas: $\overline{\tau} = \sum_i f_i \, \tau_i$ or $f_i = \frac{a_i \tau_i}{\sum a_i \tau_i}$. The average litetine in acetonitrile was found to be longer than in other solvents.

According to the EPR spectra of the $[Co(tmphen)_3](PF_6)_2$ complex (Fig. 8), the Co^{2+} ion forming the complex has a d^7-electron configuration. The spectrum confirms that the complex is not an ideal octahedron, but is symmetrical in axial directions and differs along the z-axis, that is the Jahn-Teller distortion is observed. Based on this, it can be concluded that the central ion is located in the tetragonal ligand field, not in the isotropic field. The high molar extinction coefficient in the electronic absorption spectrum of the complex also confirms this idea (i.e., the complex is not centrosymmetric).

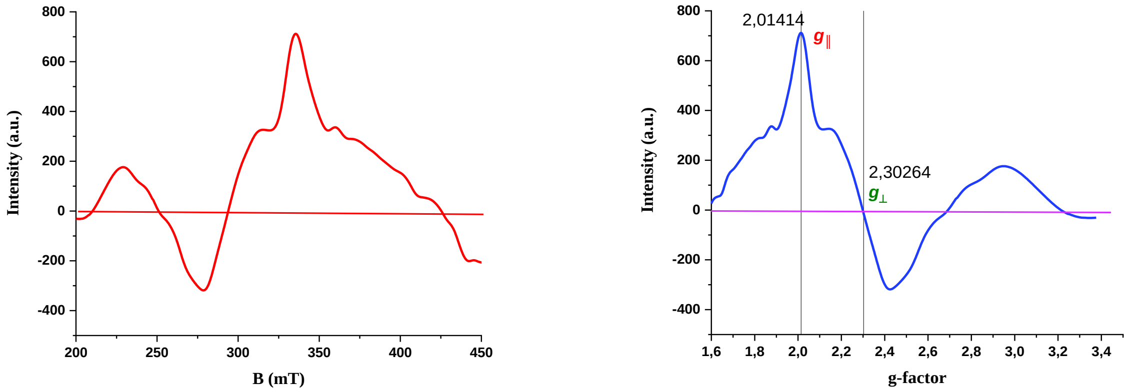
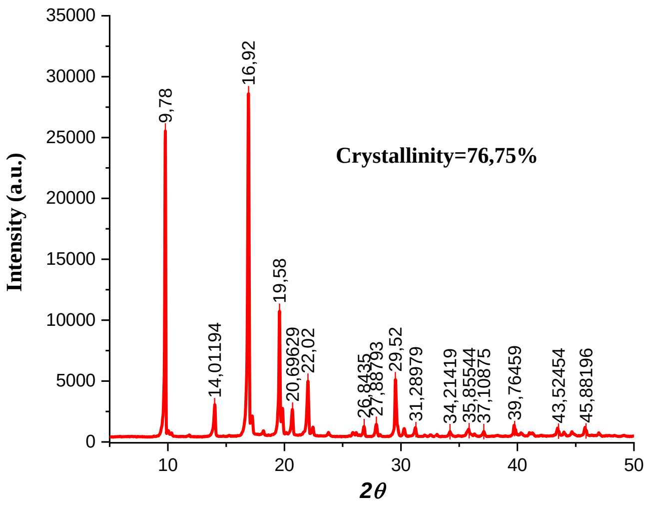


Figure 8. EPR spectrum of $[Co(tmphen)_3](PF_6)_2$ complex

The differences in the g factor, such as 2.01414 and 2.30264, are due to the anisotropic field structure of the complex and the effects of orbital moments. These differences arise due to the interaction of the electron spin moment and orbital moments, as well as tetragonal symmetry or asymmetry. These differences in the EPR spectrum indicate the effects of energy levels and magnetic fields, leading to changes in the g factor.

The diffraction pattern of $[Co(tmphen)_3](PF_6)_2$ exhibits peaks at appropriate Bragg angles, which allow the determination of the crystal structure and dimensions of the complex. The peaks from the diffractogram were used to determine the crystal phases and degree of crystallinity of the complex. The main peaks characteristic of the Co(II) complex structure in the diffraction pattern of $[Co(tmphen)_3](PF_6)_2$ can be seen in Figure 9:



Parameters	**$[Co(tmphen)_3](PF_6)_2$**
a, Å	13.215
b, Å	17.823
c, Å	19.823
α, ^{0}	90º
β, ^{0}	96.8º
γ, ^{0}	90º
V, $Å^3$	4636.1
F. G.	P21/n
Crystal system	Monoclinic

Figure 9. Diffraction pattern of $[Co(tmphen)_3](PF_6)_2$ complex

In Figure 9, the measurements were performed at room temperature and the diffraction angle (2θ) was scanned in a step mode from 5° to 50°.

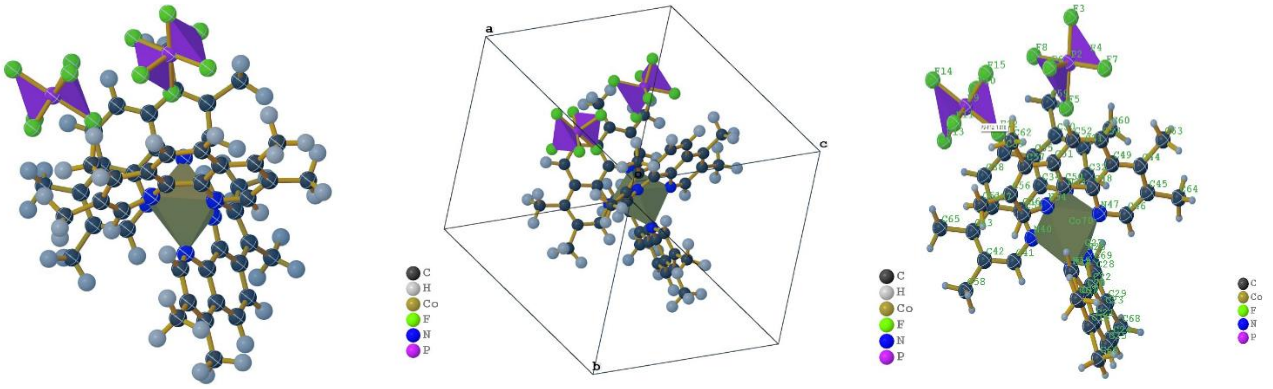


Figure 10. View of the crystal structure of the complex $[Co(tmphen)_3](PF_6)_2$ along the a,b,c axes

The crystal structure of the complex containing $[Co(tmphen)_3](PF_6)_2$ in Figures 9 and 10 is in the monoclinic, space group: P21/n. The lattice parameters are a=13.215 Å, b=17.823 Å, c=19.823 Å, and the density is ρ=1.678 g/cm^3. The angles $\alpha=\gamma=90º$, $\beta=96.8º$. Also, when calculating the crystallinity of the complex $[Co(tmphen)_3](PF_6)_2$, it was found that it has a 76.75% crystalline and 23.25% amorphous structure.

The crystal structure of the complex [Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ is triclinic, space group P1. The lattice parameters are a = 11.8123 Å, b = 13.0356 Å, c = 17.575 Å, and the density is ρ = 1.662 g/cm^3. The angles α = 91.461°, β = 101.347°, and γ = 99.830 (Figure 12).

Parameters	[Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$
a, Å	11.8123
b, Å	13.0356
c, Å	17.575
α, ^{0}	91.461
β, ^{0}	101.347
γ, ^{0}	99.830
V, Å3	2609.5
F. G.	P1
Crystal system	Triclinic

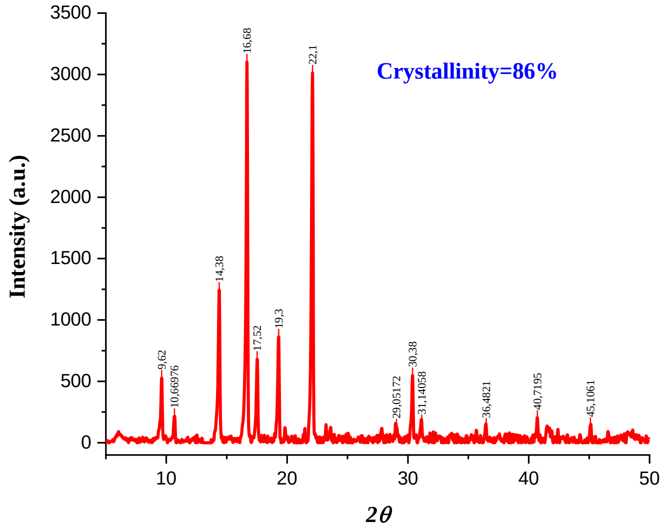


Figure 11. Diffraction pattern of [Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ complex

X-ray diffraction studies showed that the [Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ complex has an 86% crystalline and 14% amorphous structure. The high degree of crystallinity of this complex confirms that the proposed synthesis method is suitable for obtaining such complexes (Figure 11).

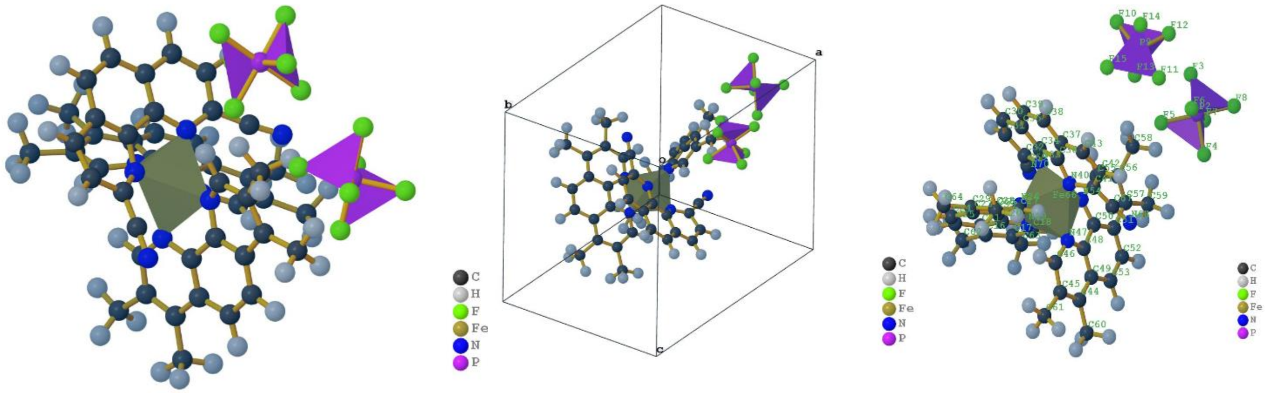


Figure 12. View of the crystal structure of the complex [Fe(tmphen)$_2$(dcbyp)](PF$_6$)$_2$ along the a,b,c axes

Thermal study of the properties of complex compounds provides important information such as the nature and number of ligands in them, as well as the thermal stability of the complex compound. The analyses were carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal studies of the [Fe(tmpen)$_2$(dcbyp)](PF$_6$)$_2$ complex were conducted in the temperature range from 55 °C to 675 °C (Figure 13).

In the DSC curves of the thermogram of the complex, an endothermic process was observed at 420-580 °C, which corresponds to the decomposition temperature of this complex at 500 °C. The complex [Fe(tmpen)$_2$(dcbyp)](PF$_6$)$_2$·nH$_2$O was dehydrated at about 100 °C to form the complex [Fe(tmpen)$_2$(dcbyp)](PF$_6$)$_2$. In the temperature range of 135-315 °C, 6,6 - dicyano-2,2-bipyridine (dcbyp) was released, with a mass loss of 4.8%. In the temperature range of 320-470 °C, 1 mol of 3,4,7,8-tetramethyl-1,10-phenanthroline was released, with a mass loss of 5.1%. The next mass loss occurred at 475-515 °C, with a turn in the curve. This corresponds to the loss of a second mole of 3,4,7,8-tetramethyl-1,10-phenanthroline, and the mass loss is 6.2%. In the TGA curve, the mass loss is 3% in the range of 520-675 °C, corresponding to the loss of one molecule of fluorine gas from the hexafluorophosphate molecule and the remaining tetrafluorophosphate anion. The final product of the thermolysis is PF_5^- anion and FeO. Using the DSC results, the enthalpy change for the same process was 353 kJ/mol (Figure 14).

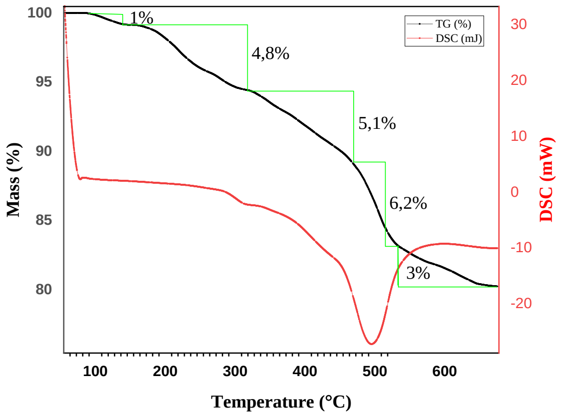


Figure 13. Derivatogram of [Fe(tmpen)$_2$(dcbyp)](PF$_6$)$_2$ complex.

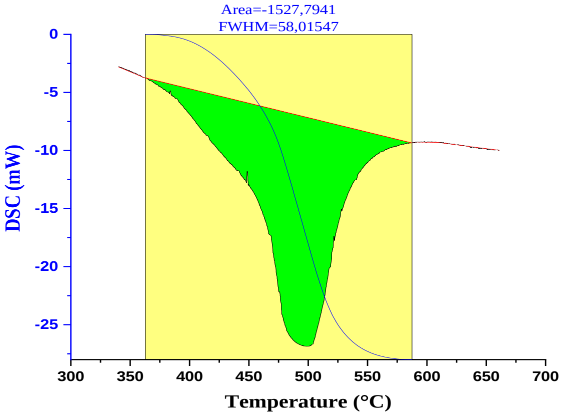


Figure 14. Enthalpy calculation from the thermal effect in [Fe(tmpen)$_2$(dcbyp)](PF$_6$)$_2$ complex.

Quantum chemical evaluation of the structure of the synthesized complexes. The structure of the complexes was analyzed quantum chemically and information about several selected orbitals is given in Table 2. The HOMO and near-HOMO orbitals (HOMOs) are mainly composed of d-orbitals of the central iron. The set of LUMOs is mainly composed of ligands. The shape of the HOMO and LUMO orbitals is shown in Figure 15, which shows that the HOMO orbitals are degenerate and mainly consist of d_{z^2} and $d_{x^2-y^2}$ orbitals of the metal. The LUMO is composed of p-orbitals of the ligands. Table 3 shows the HOMO and LUMO orbitals of the complexes of iron with three different ligands for comparison.

Table 2.

Compound	HOMO (eV)	LUMO (eV)	E_g (eV)
$[Fe(phen)_3]^{2+}$	-11.34	-7.469	3.87
$[Fe(Br_2phen)_3]^{2+}$	-11.66	-7.795	3.87
$[Fe(tmphen)_3]^{2+}$	-10.48	-6.710	3.77
$[Co(phen)_3]^{2+}$	-10.87	-7.514	3.36
$[Co(tmphen)_3]^{2+}$	-11.28	-7.844	3.44
$[Ni(phen)_3]^{2+}$	-10.94	-7.630	3.31
$[Ni(Br_2phen)_3]^{2+}$	-11.34	-7.967	3.37
$[Ni(tmphen)_3]^{2+}$	-10.13	-6.757	3.37

Table 3.

	$Fe(phen)_3]^{2+}$	$Fe(Br_2phen)_3]^{2+}$	$Fe(tmphen)_3]^{2+}$
HOMO			
M	77.83	41.72	72.40
L1	7.30	18.50	9.48
L2	6.95	19.41	9.26
L3	7.92	20.37	8.86
LUMO			
M	9.36	12.88	10.45
L1	30.25	3.33	46.12
L2	26.98	43.19	2.70
L3	33.41	40.60	40.73

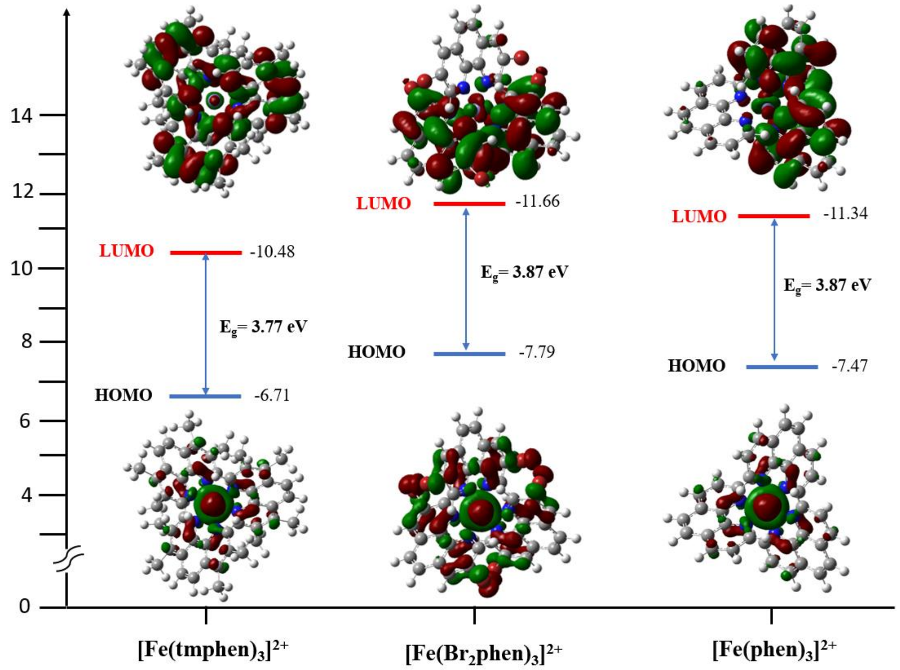


Figure 15. Difference in HOMO and LUMO energies in different iron-based complexes. Comparison of HOMO and LUMO compositions of complexes with iron as the central ion. (L –ligandlar, M – Fe)

In the $Fe(Br_2phen)_3]^{2+}$ complex, most of the HOMO orbitals are located in the ligands, and the metal contribution is 41.72%. This is significantly different from the other two complexes. Because its HOMO orbitals consist mainly of pure metal orbitals (72.4%). It was found that the composition of the HOMO and LUMO orbitals in the excited state of the complex differs from that of the complex in its ground state.

The fourth chapter of the dissertation, entitled **“Application and theoretical study of homoleptic and heteroleptic complexes of Fe(II) in photosensitizers,”** presents an analysis of practical and theoretical data obtained in the study of the photosensitizing properties of the complexes.

Photosensitizing properties of the homoleptic complex $[Fe(tmphen)_3](PF_6)_2$ as follows. Open circuit voltage (V_{OC}) is the potential developed by the cell under irradiation when no current is flowing in the external circuit. Its maximum thermodynamic value is determined by the difference between the Fermi level of the ZnO material under illumination and the Nernst potential of the redox mediator, and is strongly influenced by the recombination rate of the interfacial charge - the photocurrent corresponding to the maximum power (J_{max}) - the current density at 0 potential under illumination when zero potential is applied. The evaluation of the comprehensive performance of dye-sensitized solar cells is usually expressed in two main quantities. The first is the fill factor and the cell efficiency. The fill factor (FF) and the cell efficiency (η) expressed in equations (1) and (2) can be calculated below (Figure 16).

$$\mathrm{FF} = \frac{V_{max} \cdot J_{max}}{V_{OC} \cdot J_{SC}} \qquad (1) \qquad\qquad \eta = \frac{V_{OC} \cdot J_{SC} \cdot FF}{P_U}.100 \qquad (2)$$

DSSC current and voltage dependence measurement results are given in Table 4.

Table 4.

№	Resistance R (Ohm)	Current J (mA)	Voltage U(mV)	Power $P_{max}=J_{max}\cdot U_{max}$
1	0	16.43	16	262.88
2	0.5	16.18	17	275.06
3	1	15.98	17	271.66
4	3	15.92	20	318.40
5	5	15.83	23	364.09
6	10	15.80	31	489.80
7	15	15.51	38	589.38
8	25	15.42	53	817.26
9	50	15.15	60	909.00
10	100	15.05	167	2513.35
11	200	14.88	309	4597.92
12	∞	0.00	465	0.00

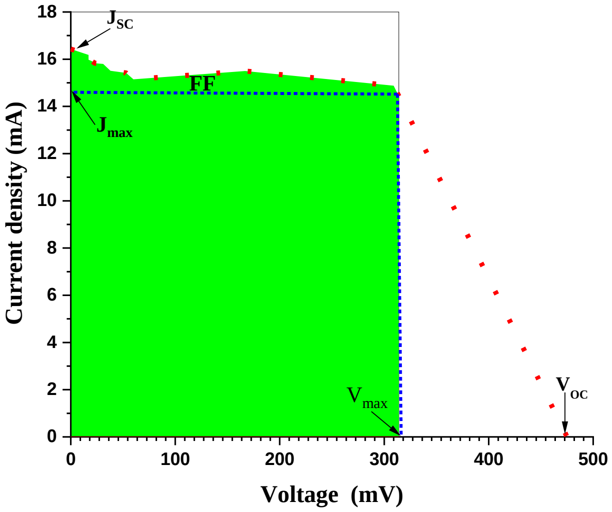


Figure 16. *J-U* relationship graph.

The following was determined from the Table 4:

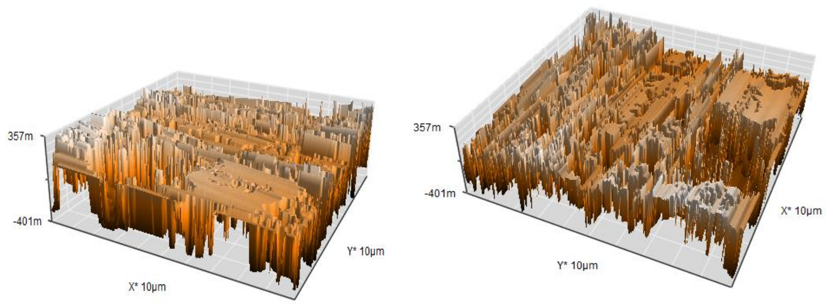
V_{OC} – 465 mV or 0.465 V
V_{max} – 309 mV or 0.309 V
J_{SC} – 16.43 mA
J_{max} – 14.88 mA
P_u – total power of illumination
FF = 0.602 (from the eq. 1)
η= 5.72% (from the eq. 2)

During this study, the conversion efficiency was 5.72% due to the use of the AM1.5G simulator. When using natural sunlight, the voltage was observed to reach 0.94 V.

When the specific resistance, voltage and current values of the heteroleptic complex $[Fe(tmphen)_2(dcbyp)](PF_6)_2$ were measured, it was found that: J_{SC} – 16.95 mA; J_{max} – 14.95 mA; V_{OC} – 485 mV; V_{max} – 330 mV; FF = 0.60. The conversion efficiency was 6.14% due to the use of the AM1.5G simulator. When using natural sunlight, the voltage was observed to reach 1.03 V.

It is known that the most commonly used material as a photoanode in DSSC is mesoporous TiO_2. A semiconductor with a large band gap energy is suitable for use as a photoanode. Good immobilization of the sensitizer on the photoanode has a positive effect on the performance of the final product. In our studies, the ZnO photoanode material was used, and its conduction band and band boundary energies are similar to those of anatase, but the electron mobility in ZnO is faster than that of TiO_2. ZnO is chemically more reactive than TiO_2, which means that it is more reactive in strong alkaline and acidic environments.

In the studies, a ZnO layer was formed as a suspension in 96% ethanol and then deposited on FTO glass. After immobilizing DSSC on the prepared layer and drying, atomic force microscopy was used to study their morphology at the nanometer scale (Figure 17).



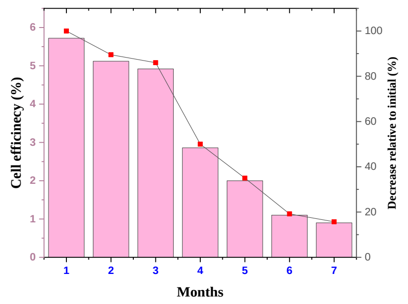


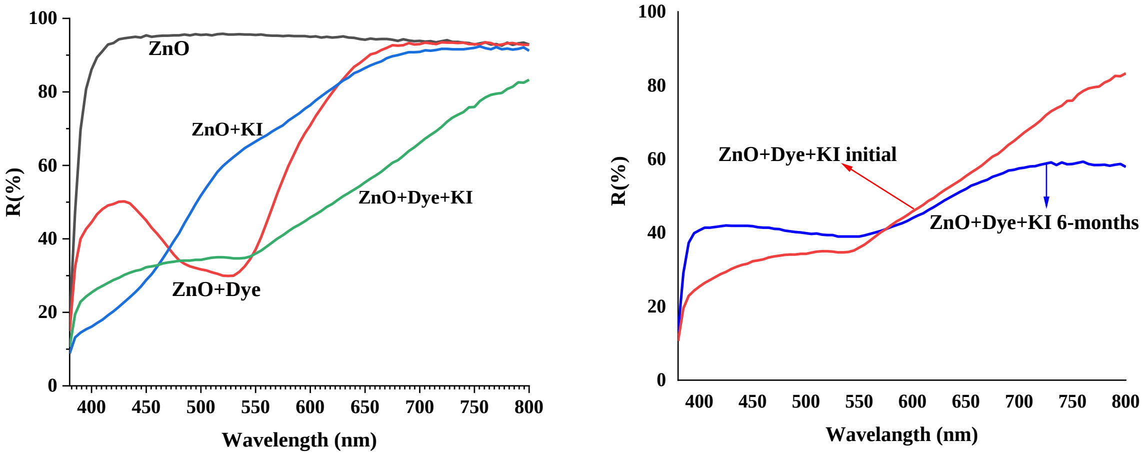
Figure 17. AFM image of surface morphology of DSSC.

Figure 18. Stability of prepared DSSC

As can be seen from Figure 17, when the image surface area of the AFM was 10 µm × 10 µm, the roughness measurement on the sample surface had a maximum peak at 357 nm and a minimum depth of 401 nm. The results show that ZnO is suitable for acting as a mesoporous photoanode for DSSC.

The results show that the prepared DSSC operates stably for 3 months, after which the useful work coefficient drops below 3% (Figure 18). This is due to the following reasons: chemical changes in ZnO under the influence of the external environment and a decrease in its adsorption capacity; decomposition of the sensitizer molecule over time; and a decrease in the DSSC performance due to a decrease in the mediator concentration.

Figure 19a shows the diffuse reflectance spectrum of the ZnO layer used as a photoanode, when the sensitizer is deposited on it, as well as when it is combined with KI and a dye. It can be seen from the spectrum that ZnO does not absorb visible light in a wide range from 430 nm to 800 nm, and therefore is suitable as a photoanode material. It was observed that all substances retained their photochemical properties when KI was added as a mediator, when the sensitizer was added, and when the mediator and dye were added. This confirms that all substances were physically adsorbed on the semiconductor ZnO materials in DSSC.



a) b)

Figure 19. Diffuse reflectance spectra of a) ZnO, KI@ZnO, Dye@ZnO, KI+Dye@ZnO; b) freshly prepared and after 6 months KI+Dye@ZnO.

Figure 19b shows the diffuse reflectance spectrum of the freshly prepared and material after 6 months. It can be seen from the spectrum that the decrease in DSSC stability is mainly caused by the sensitizer (dye) and the mediator.

CONCLUSION

1. 32 new homoleptic and heteroleptic complexes of Fe(II), Co(II), Ni(II) ions with organic ligands (6,6-dicyano-2,2-bipyridine, 3,8-dibromo-1,10-phenanthroline, 2,2-biquinoline, 3,4,7,8-tetramethyl-1,10-phenanthroline) and in the presence of water and alcohol molecules were synthesized. Their composition, structure, coordination through N (nitrogen) donor atoms in organic ligands, and the electronic configuration of the central atoms consisting of a modified octahedron were determined using EPR, electronic absorption, FTIR, and Raman spectra.

2. The electronic and geometric structures, energetic parameters, and theoretical coordination centers of the ligands were determined by quantum chemical calculations using the Gaussian 16W program DFT method, and the semiconductor properties of the complexes were determined based on the difference in HOMO and LUMO energies.

3. The luminescence lifetime of the synthesized complexes was longer in acetonitrile than in other solvents, i.e. $[Fe(tmphen)_3]^{2+}$ $\tau=9$ ns, $[Fe(tmphen)_2(dcbyp)]^{2+}$ $\tau=10$ ns, as measured on a pico Quant spectrofluorometer. The emission spectrum was determined to be due to metal-to-ligand charge transfer (MLCT). According to the EPR spectrum analysis of the $[Co(tmphen)_3](PF_6)_2$ complex, it is not an ideal octahedron, but symmetrical in axial directions, and the Jahn-Teller distortion is observed along the z-axis. According to the diffraction pattern analysis, the crystal structure was determined to be monoclinic.

4. The dependence of the thermal and solution stability constants of the synthesized coordination compounds on the nature of the ligands and the stability constants of the Fe(II) complexes were calculated, and according to their values, the $[Fe(tmphen)_3]^{2+}$ homoligand complex was found to be the most stable. The dependence of the $K_{instability}$ value of complexes with different homoligands on the composition and structure of the radical attached to the ring in them was explained. The reasons for the formation of endo- and exo-effects in thermograms were determined, and thermal decomposition products were determined. Also, the gradual course of thermal decomposition of the complexes and the enthalpy values for these processes were calculated.

5. Based on the data absorption and voltammetric analysis of the synthesized iron(II) homo- and heteroleptic complexes, the possibility of using them as dye-sensitized solar cells in the preparation of solar cells was determined. When using the AM1.5 simulator, the conversion efficiency was observed to reach from 5.72% to 6.14%, and from 11% to 11% when using sunlight.

6. Complex compounds of Fe(II), Co(II), Ni(II) ions with homo- and heteroligands were tested at the Russian Federation's FLUID LLC, ELKIMYO – AGROHIMOYA LLC under the Elektrokimyozavod Joint Stock Company, and BMAX BUILDING MATERIALS LLC and recommended for use in obtaining DSSC.

НАУЧНЫЙ СОВЕТ DSc.03/30.12.2019.K.01.03
ПО ПРИСУЖДЕНИЮ УЧЁНОЙ СТЕПЕНИ ДОКТОРА НАУК
ПРИ НАЦИОНАЛЬНОМ УНИВЕРСИТЕТЕ УЗБЕКИСТАНА

САМАРКАНДСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ ИМЕНИ ШАРОФА РАШИДОВА

ТОШПУЛАТОВ ДОСТОН ТОЛМАС УГЛИ

СИНТЕЗ И ФОТОХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ ГОМОЛЕПТИЧЕСКИХ И ГЕТЕРОЛЕПТИЧЕСКИХ КООРДИНАЦИОННЫХ СОЕДИНЕНИЙ НЕКОТОРЫХ 3d-МЕТАЛЛОВ

02.00.01– Неорганическая химия

АВТОРЕФЕРАТ ДИССЕРТАЦИИ ДОКТОРА ФИЛОСОФИИ (PhD)
ПО ХИМИЧЕСКАМ НАУКАМ

Ташкент – 2025

Тема диссертации доктора философии (PhD) зарегистрирована в Высшей аттестационной комиссии при Министерстве высшего образования, науки и инноваций Республики Узбекистан номером B2021.1.PhD/K380.

Диссертация выполнена в Национальном университете Узбекистана.

Автореферат диссертации на трех языках (узбекский, английский, русский, (резюме)) размещен на веб-странице Научного совета (www.ik-kimyo.nuuz.uz) и на информационно-образовательном портале “Ziyonet” по адресу (www.ziyonet.uz).

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Защита диссертации состоится “17” апрель 2025 г. в “14^{00}” часов на заседании Научного совета DSc.03/30.12.2019.K.01.03 при Национальном университете Узбекистана. (Адрес: 100174, г. Ташкент, ул. Университетская 4. Тел.: (99871) 227-12-24; факс: (99824) 246-02-24; e-mail: ilmiy_kengash@nuu.uz).

С диссертацией можно ознакомиться в Информационно-ресурсном центре Национального университета Узбекистана за (зарегистрировано за №47) (Адрес:100174, г. Ташкент, Университетская 4. Тел.: (99871) 227-12-24; факс: (99824) 246-02-24; e-mail: nauka@nuu.uz.

Автореферат диссертации разослан “04” апрель 2025 г.
(реестр протокол рассылки № 12 от “03” апрель 2025 г.).

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ВВЕДЕНИЕ (аннотация диссертации доктора философии (PhD))

Цель исследования заключается в синтезе гомолептических и гетеролептических комплексных соединений ионов Fe(II), Co(II) и Ni(II) в присутствии органических лигандов и изучении фотохимических свойств полученных соединений.

Объектом исследования является производные 2,2-бипиридина и 1,10-фенантролина, их комплексы с солями Fe(II), Co(II), Ni(II), стеклами FTO и ZnO.

Научная новизна исследования заключается в следующем:

синтезировано 32 новых гомолептических и гетеролептических комплексов ионов Fe(II), Co(II), Ni(II) с органическими лигандами (6,6 – дициано-2,2-бипиридин, 3,8-дибром-1,10-фенантролин, 2,2-биксинолин, 3,4,7,8-тетраметил-1,10-фенантролин) в присутствии дополнительных молекул воды и спирта;

определены значения констант устойчивости гомолептических комплексов, образующихся в растворе с ионами Fe(II) в присутствии 2,2-бипиридина, 6,6–дициано-2,2-бипиридина, 3,4,7,8-тетраметил-1,10-фенантролина, и их зависимость от природы лигандов;

с использованием усовершенствованных программ квантово-химических методов определены геометрические и энергетические параметры, распределение зарядов в атомах и реакционные центры синтезированных сложных молекул;

с использованием результатов ДСК определены термические свойства синтезированных комплексов, механизм термического разложения и их количественные, энергетические аспекты, а также изменение энтальпии для тех же процессов;

энергия электронного перехода синтезированного комплекса была рассчитана методом Тауца для состояний $(\alpha h\nu)^2$ и $(\alpha h\nu)^{1/2}$, исходя из пригодности СКСЭ для сенсибилизаторов ввиду их полупроводниковой природы;

установлено, что фотосенсибилизирующие свойства синтезированных комплексов с гомо- и гетеролептическими лигандами ионов Fe(II) составляют 5,72% - 6,14% при использовании имитатора AM1.5G, а при естественном солнечном свете достигают 11% - 12%.

Внедрение результатов исследования. На основе полученных научных результатов по получению неорганических комплексных соединений для солнечных элементов:

Внедрен в практику в ООО «ЭЛКИМЁ – АГРОХИМОЯ» при совместного предприятия «Электрокимёзавод» (справка №92 СП АО «Электрокимёзавод» от 06.05.2024 г.). Образует окрашенные комплексы с производными 2,2-бипиридина и 1,10-фенантролина, содержащими ионы Fe^{2+}, Co^{2+}, Ni^{2+}, что позволяет определять наличие целевых молекул при низких концентрациях ионов 3d-металлов до 0,0025 моль/л. Включен в программу инновационного развития АО «Электрокимёзавод» на 2026-2028 годы;

Реализовано в совместном предприятии ООО «БМАКС СТРОИТЕЛЬНЫЕ МАТЕРИАЛЫ» (Справка №74/А ООО «БМАКС СТРОИТЕЛЬНЫЕ МАТЕРИАЛЫ» от 05.04.2024 г.). Установлено, что 3 гомолептических и 4 гетеролептических комплекса иона Fe(II); 5 гомолептических и 8 гетеролептических комплексов иона Co(II); 5 гомолептических и 7 гетеролептических комплексов иона Ni(II) при использовании для сенсибилизированных красителями солнечных элементов обладают фотосенсибилизирующими свойствами и высоким коэффициентом усвоения красителей.

Реализовано в совместном предприятии ООО «ФЛЮИД» Российской Федерации (Справка ООО «ФЛЮИД» № 94 от 03.04.2024 г.). Гомолептичность 3d-металлов $[Fe(L_1)_3](PF_6)_2$, $[Co(L_1)_3](PF_6)_2$, $[Ni(L_1)_3](PF_6)_2$, $[Fe(L_4)_3](PF_6)_2$, $[Co(L_4)_3](PF_6)_2$, $[Ni(L_4)_3](PF_6)_2$; Гетеролептические комплексы $[Co(L_1)(L_2)_2](PF_6)_2$, $[Fe(L_4)_2(L_1)](PF_6)_2$, $[Co(L_1)(L_4)_2](PF_6)_2$, $[Ni(L_1)(L_4)_2](PF_6)_2$, $[Ni(L_1)(L_2)_2](PF_6)_2$, $[Ni(L_1)_2(L_4)](PF_6)_2$ были использованы для сенсибилизированных красителями солнечных элементов, и было обнаружено, что красители обладают фотосенсибилизирующими свойствами и высокими коэффициентами поглощения.

Структура и объем диссертации. Диссертация состоит из введения, 4 глав, заключения, списка использованных литератур и приложения. Объем диссертации составляет 120 страниц.

E’LON QILINGAN ISHLAR RO‘YXATI
СПИСОК ОПУБЛИКОВАННЫХ РАБОТ
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I bo‘lim (I часть; I part)

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II bo‘lim (II часть; II part)

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Avtoreferat Sharof Rashidov nomidagi Samarqand davlat universiteti
“Ilmiy axborotnoma” jurnali tahririyatida tahrirdan o‘tkazilib o‘zbek, ingliz va rus
tillaridagi matnlari o‘zaro muvofiqlashtirildi (02.04.2025 yil).

Bosmaxona tasdiqnomasi:

4268

2025-yil 3-aprelda bosishga ruxsat etildi:
Ofset bosma qog‘ozi. Qog‘oz bichimi $60x84_{1/16}$.
“Times new roman” garniturasi. Raqamli bosma usuli.
Hisob-nashriyot t.: 2,8. Shartli b.t. 2,4.
Adadi 100 nusxa. Buyurtma №04/04.

SamDCHTI tahrir-nashriyot bo‘limida chop etildi.
Manzil: 140104, Samarqand sh., Bo‘stonsaroy ko‘chasi, 93.