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Synthesis, characterization and application of Ru(II) complexes containing pyridil ligands for dye-sensitized solar cells

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In this research, a series of Ru(II) complexes, ([Ru(1-7)(ina)$(NCS)_2$] (1-7=5-[6-(5-mercapto-1,3,4-oxadiazol-2-yl)pyridin-2-yl]-1,3,4-oxadiazole-2-thiol's, ina=isonicotinic acid) were synthesized and characterized using different spectroscopic and analytic techniques, such as NMR, UV, IR, CV and CHN. Also, the new complexes were used in dye-sensitized solar cells (DSSC) as sensitizers. Current-voltage characteristics showed that the modifications of ligands clearly affected DSSC yield. Additionally, DFT calculations were performed and showed locations of frontier molecular orbitals of the complexes. While the locations of HOMO and HOMO – 1 orbitals are on Ru(II) metal center and SCN^- ligands, the location of LUMO and LUMO + 1 orbitals are on the 1-7 ligands.

Keywords: *Ru(II) complexes; dye-sensitized solar cells (DSSCs); sensitizer; DFT; current-voltage characteristics*

1. Introduction

1,3,4-oxadiazole-2(3H)-thione skelaton composed of easily synthesized organic groups is used in many species showing anticancer [1], antimicrobial [2], antioxidant [3] activities. Additionally, this group has a good potential for complaxation with transition metals. For example, Gudasi et al. [4] synthesized 5-[6-(5-mercapto-1,3,4-oxadiazol-2-yl)pyridin-2-yl]-1,3,4-oxadiazole-2-thiol compound and some of its transition metal complexes, and investigated their biological activity.

Ruthenium as a transition metal has gained a growing interest in the literature. Especially, Ru(II) complexes have been used for many applications such as catalysis, medicinal chemistry, photovoltaics, etc. [5–20]. The success of these complexes depends on ligand characteristics (electron donation and steric hindrance) [21–26]. There is a lot of research about the advantages of the Ru(II) complexes including pyridyl type ligands in the photovoltaic applications [27–34].

Dye-sensitized solar cells (DSSC) are the focus of interest because of their low cost and easy production [35–37]. Until now, many organic and inorganic dyes have been used as sensitizers [38–42]. Most successful sensitizers include Ru(II)-based complexes containing poly-pyridyl ligands. The poly-pyridyl ligands in such Ru(II) complexes were used as both ancillary and anchor ligands. As anchor ligands, poly-pyridyl ligands frequently contain –COOH group such as 2 2'-bipyridine-4 4'-dicarboxylic acid (dcby). On the other hand, for the same purpose, the use of isonicotonic acid (ina) which is a simple analog of dcby is very rare [43–45]. Recently, we have shown that Ru(II) complexes containing ina ligand have good efficiency as sensitizers [46]. As ancillary ligand, pyridine-based ligands are broadly used in DSSC because of simple preparation of their derivatives [36, 47].

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However, there is a request for the synthesis of novel and efficient Ru(II) complexes for DSSC both in theoretical studies and industry.

In this work, new Ru(II) complexes containing 5-[6-(5-mercapto-1,3,4-oxadiazol-2-yl)pyridin-2-yl]-1,3,4-oxadiazole-2-thiol ligands were synthesized and used as the sensitizers for DSSC. The current-voltage characteristics of DSSCs were monitored under different illumination conditions.

2. Experimental

All chemicals were obtained from commercial suppliers and were used as purchased. Standard Schlenk technique was used for synthesis. The 5,5'-(pyridine-2,6-diyl)di(1,3,4-oxadiazole-2-thiol) (**1**) was synthesized in the literature [2] using:

General synthesis of 2-7

The S-alkylation products (**2-7**) of 5,5'-(pyridine-2,6-diyl)di(1,3,4-oxadiazole-2-thiol) were prepared by modification of the literature method [48]. The **1** (1.51 mmol) and KOH (3.02 mmol) were stirred in acetone (10 mL) for 2 h at 100 °C. After this time, appropriate alkyl halide (3.00 mmol) was added and mixed for another 24 h under reflux conditions. The volatiles were removed under vacuum. The residue was extracted with DCM/H_2O and the organic layer was dried with $MgSO_4$. The product was crystallized with methanol.

2,6-bis[5-(methylsulfanyl)-1,3,4-oxadiazol-2-yl]pyridine (2)

Yield: 51 %. ^{1}H–NMR (400 MHz, DMSO–d_6) δ ppm 2.80 (s, 6 H, 2 x – CH_3) 8.27 – 8.34 (m, 3 H, Py–H). ^{13}C–NMR (101 MHz, DMSO–d_6) δ ppm 18.59 (–CH_3); 124.87; 139.81; 143.06; 163.92; 166.41. FT-IR (cm^{-1}): 3072 (νC–H_{arom}), 3013 (νC–H_{arom}), 2971 (νC–$H_{aliph.}$), 2929 (νC–$H_{aliph.}$), 1591 (νC=N), 1580, 1547, 1505, 1463, 1452, 1441, 1366, 1314, 1229, 1205, 1161, 1102, 1073, 990, 977, 956, 898, 822, 778, 735, 701, 653, 595, 539, 528, 519, 429, 408.

2,6-bis[5-(ethylsulfanyl)-1,3,4-oxadiazol-2-yl]pyridine (3)

Yield: 27 %, m.p: oily product. ^{1}H–NMR (400 MHz, $CDCl_3$) δ ppm 1.54 (t, J = 7.33 Hz, 6 H, 2 x – CH_3) 3.38 (q, J = 7.33 Hz, 4 H, 2 x – CH_2) 8.06 (t, J = 7.79 Hz, 1 H, Py–H_p) 8.33 (d, J = 7.79 Hz, 2 H, 2 x Py–H_m). ^{13}C–NMR (101 MHz, DMSO–d_6) δ ppm 14.94 (–CH_3); 28.69 (–CH_2); 125.32; 140.30; 143.52; 164.37; 166.86. FT-IR (cm^{-1}): 3062 (νC–H_{arom}), 2970 (νC–$H_{aliph.}$), 2931 (νC–$H_{aliph.}$), 2870, 1635 (νC=N), 1590, 1563, 1533, 1464, 1432, 1417, 1374, 1357, 1268, 1198, 1162, 1125, 1061, 999, 969, 957, 905, 837, 775, 758, 700, 646, 567, 494, 429.

2,6-bis[5-(decylsulfanyl)-1,3,4-oxadiazol-2-yl]pyridine (4)

Yield: 63 %, m.p: 75–77. ^{1}H–NMR (400 MHz, DMSO–d_6) δ ppm 0.72 – 0.85 (m, 6 H, 2 x – CH_3) 1.09 – 1.43 (m, 28 H, decyl-CH_2-) 1.51 – 1.85 (m, 4 H, decyl-CH_2–) 4.00 – 4.34 (m, 4 H, decyl-CH_2-) 8.16 – 8.33 (m, 3 H, Py–H). ^{13}C–NMR (101 MHz, DMSO–d_6) δ ppm 14.46 (–CH_3), 22.61 (–CH_2), 26.00 (–CH_2), 28.32 (–CH_2), 29.40 (–CH_2), 31.80 (–CH_2), 32.66 (–CH_2), 34.66 (–CH_2), 125.70, 140.56, 145.12, 161.01, 164.91. FT-IR (cm^{-1}): 3082 (νC–H_{arom}), 2953 (νC–$H_{aliph.}$), 2917 (νC–$H_{aliph.}$), 2849, 1644 (νC=N), 1591, 1548, 1470, 1456, 1422, 1355, 1256, 1202, 1187, 1164, 1104, 1073, 1019, 975, 828, 778, 740, 721, 706, 653.

2,6-bis[5-(benzylsulfanyl)-1,3,4-oxadiazol-2-yl]pyridine (5)

Yield: 56 %. ^{1}H NMR (400 MHz, DMSO–d_6) δ ppm 4.60 (s., 4 H, Bezyl-CH_2) 7.28 – 7.51 (m, 10 H, Arom.-CH) 8.15 – 8.29 (m., 3 H, Py-H). ^{13}C NMR (100 MHz, DMSO–d_6) δ ppm 36.42 (Bezyl-CH_2), 125.32, 128.26, 129.03, 129.60, 136.79, 140.24, 143.42, 164.42, 165.49. FT-IR (cm^{-1}): 3274, 3085 (νC–H_{arom}), 3060 (νC–H_{arom}), 3028 (νC–H_{arom}), 2933 (νC–$H_{aliph.}$), 1637 (νC=N), 1592, 1494, 1464, 1452, 1239, 1199, 1158, 1101, 1070, 1027, 998, 916, 839, 819, 763, 735, 694, 650, 565, 471, 458, 425.

2,6-bis[5-(2,3,5,6-tetramethylphenylsulfanyl)-1,3,4-oxadiazol-2-yl]pyridine (6)

Yield: 56 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.18 – 2.42 (m, 24 H, 8 x–CH_3) 4.73 (d, J = 2.29 Hz, 4 H, Bezyl-CH_2) 6.97 (s, 2 H, Arom.-CH) 8.09 (t, J = 8.01 Hz, 1 H, Py–H_p) 8.38 (d, J = 7.79 Hz, 2 H, Py–H_m). ^{13}C NMR (101 MHz, DMSO–d_6) δ ppm 15.51 (–CH_3),

20.45 (–CH_3), 42.06 (Bezyl-CH_2), 130.02, 131.55, 133.38, 133.38, 133.79, 134.11, 134.29, 143.91, 164.05, 166.92. FT-IR (cm^{-1}): 3085 (νC–H_{arom}), 3020 (νC–H_{arom}), 3004(νC–H_{arom}) , 2964 (νC–$H_{aliph.}$), 2941 (νC–$H_{aliph.}$), 2919 (νC–$H_{aliph.}$), 1613 (νC=N), 1591, 1579, 1462, 1418, 1395, 1384, 1309, 1259, 1220, 1202, 1158, 1124, 1097, 1068, 1013, 995, 960, 896, 867, 837, 792, 749, 703, 675, 618, 601, 529, 460, 421.

2,6-bis[5-(pentafluorophenylsulfanyl)-1,3,4-oxadiazol-2-yl]pyridine (7)

Yield: 68 %. ^{1}H NMR (400 MHz, CDCl3) δ ppm 4.64 (s, 4 H, Bezyl-CH_2) 8.11 (t, J = 7.79 Hz, 1 H, Py–H_p) 8.37 (d, J = 7.79 Hz, 2 H, Py–H_m). ^{13}C NMR (101 MHz, DMSO–d_6) δ ppm 24.50 (Bezyl-CH_2), 111.57, 125.68, 136.26, 138.74, 140.46, 143.43, 146.65, 164.14, 164.92. FT-IR (cm^{-1}): 3277, 300 7(νC–H_{arom}), 2934 (νC–$H_{aliph.}$), 2857, 1656 (νC=N), 1592, 1578, 1520, 1504, 1472, 1441, 1313, 1290, 1255, 1207, 1190, 1164, 1125, 1080, 1038, 988, 964, 876, 826, 776, 734, 701, 645, 619, 560, 456.

General synthesis of C1-7

The **1-7** (0.326 mmol), $[RuCl_2(p–cymene)]_2$ (0.163 mmol), isonicotinic acid (0.326 mmol) and NH_4SCN (1.304 mmol) were stirred in DMF (10 mL) at 110 °C for 24 h. After of this time, the product was precipitated with diethyl ether. The residue was filtered and washed with pure water, ethanol and diethyl ether.

C1

Yield: 86 %, m.p > 280 °C. ^{1}H–NMR (400 MHz, DMSO–d_6) δ ppm 7.82 (d, J=5.95 Hz, 2 H, ina-CH) 8.17 – 8.28 (m, 3 H, Py–H) 8.78 (d, J = 5.95 Hz, 2 H, ina-CH). ^{13}C–NMR (101 MHz, DMSO–d_6) δ ppm 123.41; 142.84; 147.66; 150.70; 150.95; 159.37; 166.61; 177.04; 178.47. FT-IR (cm^{-1}): 3440 (νO–H), 3182, 3056 (νC–H_{arom}), 2926, 2872, 2102 (νCN), 1720 (νC=O), 1679, 1610 (νC=N), 1503, 1407, 1365, 1284, 1197, 1160, 1122, 1075, 1057, 1029, 1005, 991, 934, 863, 815, 803, 784, 770, 734, 687, 656, 633, 590, 566, 521, 471, 435, 417. Anal. Calc. for **$C_{17}H_{10}N_8O_4RuS_4.5H_2O$ [709.72]**: C, 28.8; H, 2.8; N, 15.8; found: C, 28.7; H, 2.7; N, 15.0 %. Positive ESI-MS (m/z): 620.3 (619.9) $[M]^+$

C2

Yield: 48 %, m.p > 280 °C. ^{1}H–NMR (400 MHz, DMSO–d_6) δ ppm 2.49 (s, 6 H, 2 x – CH_3) 7.72 (d, J = 5.95 Hz, 1 H, ina-CH) 8.05 (d, J = 5.50 Hz, 2 H, Py–H_m) 8.11 (m, 1 H, Py–H_p) 8.32 (d, J = 5.95 Hz, 1 H, ina-CH) 8.77 – 8.89 (m, 2 H, ina-CH). ^{13}C–NMR (101 MHz, DMSO–d_6) δ ppm 34.71 (–CH_3); 122.80; 123.76; 130.28; 131.46; 133.28; 140.05; 156.44; 156.44; 156.93; 166.91. FT-IR (cm^{-1}): 3374 (νO–H), 3004 (νC–H_{arom}), 2963 (νC–$H_{aliph.}$), 2926 (νC–$H_{aliph.}$), 2099 (νCN), 1956, 1712 (νC=O), 1605 (νC=N), 1575, 1540, 1464, 1415, 1373, 1322, 1253, 1202, 1131, 1092, 1078, 1052, 1019, 950, 886, 859, 841, 782, 772, 753, 696, 662, 611, 514, 418. Anal. Calc. for $C_{19}H_{14}N_8O_4RuS_4.5H_2O$ [737.77]: C, 30.9; H, 3.3; N, 15.2; found: C, 31.1; H, 3.6; N, 15.3 %. Positive ESI–MS (m/z): 647.9 (647.8) $[M]^+$

C3

Yield: % 69, m.p > 280 °C. ^{1}H–NMR (400 MHz, DMSO–d_6) δ ppm 1.09 – 1.43 (m, 6H, 2 x – CH_3) 4.14 – 4.51 (m, 4 H, 2 x – CH_2) 7.63 – 7.72 (m, 1 H, ina-CH) 7.87 – 7.98 (m, 2 H, Py–H_m) 8.07 – 8.16 (m, 2 H, Py–H_p + ina-CH) 8.65 – 8.84 (m, 2 H, ina-CH). ^{13}C–NMR (101 MHz, DMSO–d_6) δ ppm 34.68 (-CH_3); 42.87 (–CH_2); 123.32; 124.68; 130.15; 133.58; 139.70; 149.54; 151.06; 156.18; 165.86. FT-IR (cm^{-1}):3397 (νO–H), 3073 (νC–H_{arom}), 2924 (νC–$H_{aliph.}$), 2101 (νCN), 1681 (νC=O), 1604 (νC=N), 1575, 1498, 1466, 1416, 1378, 1261, 1222, 1205, 1136, 1093, 1076, 1051, 1020, 1000, 951, 906, 868, 843, 785, 771, 752, 724, 684, 644, 613, 513, 461. Anal. Calc. for $C_{21}H_{18}N_8O_4RuS_4$.DMF [895.03]: C, 38.5; H, 3.4; N, 16.8; found: C, 38.4; H, 3.6; N, 16.9 %. Positive ESI-MS (m/z): 675.9 (675.6) $[M]^+$

C4

Yield: 32 %, m.p:196 °C (dec.). ^{1}H–NMR (400 MHz, DMSO–d_6) δ ppm 0.99 – 1.24 (m, 38 H, decyl-CH) 4.31 (t, J = 4.81 Hz, 4 H, decyl-CH_2-) 7.55 – 7.76 (m, 2 H, ina-CH) 8.04 – 8.15 (m, 2 H, Py–H_m) 8.48 (t, J = 8.24 Hz, 1 H, Py–H_p) 8.72 – 8.77 (m, 2 H, ina-CH). ^{13}C–NMR (101 MHz, DMSO–d_6) δ ppm 14.18 (–CH_3); 16.05 (–CH_2); 22.74 (–CH_2); 24.01 (–CH_2); 24.95 (–CH_2); 25.97 (–CH_2); 29.72 (–CH_2); 31.99 (–CH_2); 34.18 (–CH_2); 109.72; 125.05; 136.42; 138.89; 139.92;

143.76; 146.69; 157.59; 164.71. FT-IR (cm^{-1}): 2971 (νC–$H_{aliph.}$), 2923 (νC–$H_{aliph.}$), 2852, 2104 (νCN), 1737 (νC=O), 1599 (νC=N), 1543, 1506, 1486, 1462, 1437, 1416, 1371, 1325, 1229, 1217, 1205, 1091, 1048, 1008, 985, 851, 800, 771, 746, 697, 679, 635, 514, 440. Anal. Calc. for $C_{37}H_{50}N_8O_4RuS_4.5H_2O$ [990.25]: C, 44.9; H, 6.1; N, 11.3; found: C, 44.9; H, 6.4; N, 10.7 %. Positive ESI–MS (m/z): 899.8 (900.2) $[M]^+$

C5

Yield: 51 %, m.p: 236 °C (dec). ^{1}H–NMR (400 MHz, DMSO–d_6) δ ppm 4.57 (s, 4H, Bezyl-CH_2), 7.20 – 7.36 (m, 8 H, Arom.-CH) 7.47 (t, J = 6.64 Hz, 2 H, Arom.-CH) 7.53 – 7.60 (m, 2 H, ina-CH) 7.64 – 7.71 (m, 1 H, Py–H_p) 7.76 (d, J = 5.95 Hz, 2 H, ina-CH) 7.87 (d, J = 6.87 Hz, 2 H, Py–H_m) 8.72 (d, J = 5.95 Hz, 1 H, ina-CH) 9.96 (s, 1 H, –OH). FT-IR (cm^{-1}): 3375 (νO–H), 3052 (νC–H_{arom}), 2989 (νC–$H_{aliph.}$), 2922 (νC–$H_{aliph.}$), 2093 (νCN), 1717 (νC=O), 1651, 1602 (νC=N), 1542, 1494, 1465, 1446, 1412, 1367, 1250, 1228, 1178, 1150, 1128, 1090, 1067, 1056, 1025, 1006, 987, 966, 919, 861, 805, 768, 748, 698, 662, 565, 474, 441, 420, 407. Anal. Calc. for $C_{31}H_{22}N_8O_4RuS_4.3H_2O$ [853.93]: C, 43.6; H, 3.3; N, 13.1; found: C, 43.9; H, 3.1; N, 13.1 %. Positive ESI-MS (m/z): 798.7 (799.0) $[M\text{-}H]^+$

C6

Yield: 94 %, m.p > 280 °C. FT-IR (cm^{-1}): 3025 (νC–H_{arom}), 2989 (νC–$H_{aliph.}$), 2972 (νC–$H_{aliph.}$), 2902 (νC–$H_{aliph.}$), 2099 (νCN), 1716 (νC=O), 1648, 1604 (νC=N), 1578, 1539, 1472, 1450, 1409, 1390, 1382, 1205, 1150, 1079, 1057, 1007, 965, 865, 810, 770, 748, 697, 638, 625, 554, 502. Anal. Calc. for $C_{39}H_{34}N_8O_4RuS_4.3H_2O$ [966.15]: C, 48.5; H, 4.6; N, 11.6; found: C, 48.5; H, 4.6; N, 11.6 %. Positive ESI–MS (m/z): found (calc.) 910.8 (911.1) $[M\text{-}H]^+$

C7

Yield: 78 %, m.p > 280 °C. H–NMR (400 MHz, DMSO–d_6) δ ppm 4.30 (s, 4 H, Bezyl-CH_2) 6.98 – 7.10 (m, 2 H, Py–H_m) 7.77 (d, J = 5.95 Hz, 1 H, ina-CH) 7.81 (d, J = 6.87 Hz, 1 H, ina-CH) 8.10 – 8.15 (m, 1 H, Py–H_p) 8.51 (d, J = 6.41 Hz, 1 H, ina-CH) 8.73 (m, 1 H, ina-CH). FT-IR (cm^{-1}): 3346 (νO–H), 2989 (νC–$H_{aliph.}$), 2972 (νC–$H_{aliph.}$), 2101 (νCN), 1717 (νC=O), 1649, 1609 (νC=N), 1580, 1556, 1520, 1504, 1464, 1417, 1376, 1326, 1252, 1207, 1153, 1124, 1058, 1018, 982, 963, 860, 803, 770, 698, 673, 556, 504. Anal. Calc. for $C_{31}H_{12}F_{10}N_8O_4RuS_4.6H_2O$ [1087.88]: C, 34.2; H, 2.2; N, 10.3; found: C, 34.1; H, 2.2; N, 10.2 %. Positive ESI-MS (m/z): found (calc.) 979.8 (979.9) $[M]^{+1}$

3. Results and discussion

5,5'-(pyridine-2,6-diyl)di(1,3,4-oxadiazole-2-thiol) (**1**) was synthesized in the reaction of pyridine-2,6-dicarbohydrazide and carbon disulfide in basic media with good yield. Then, the S-alkylations of the **1** were achieved in acetone with alkyl halide and KOH. The Ru(II) complexes (**C1**-**7**) were obtained from the one-pot reaction of compound **1**-**7**, $[RuCl_2(p\text{-cymene})]_2$, as the metal precursor which is easily handleable and gives facile substitution reactions, isonicotinic acid and NH_4SCN in DMF with good yield. The reaction scheme is given in Fig. 1. The ligands (**1**-**7**) are soluble in many organic solvents (CH_2Cl_2, MeOH, DMF, DMSO, aceton, etc.) but the solubility of its Ru(II) complexes (**C1**-**7**) is poor even in polar solvents.

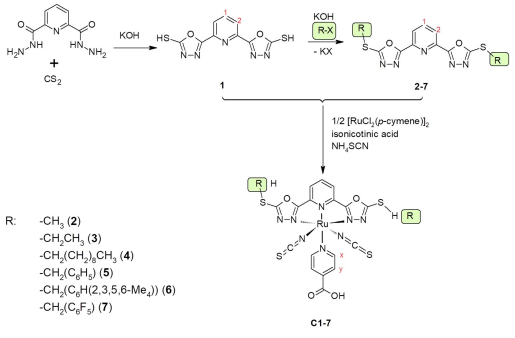

Fig. 1. Syntheses and NMR assignment of the studied compounds.

Synthesized compounds were characterized with CHN analyses and NMR, FT-IR, UV-Vis spectroscopic techniques. The satisfactory results of CHN analyses of the complexes using a LECO-CHNS–932 instrument were achieved. NMR spectra of the compounds were recorded at 297 K on a Jeol JNM-ECX400II. The $-H_{1,2}$ protons of the

1 were monitored between 8.13 ppm to 8.28 ppm as multiplet in ^{1}H–NMR spectra. After complexation, the same protons slightly shifted towards 8.17 ppm to 8.23 ppm region as multiplets for **C1**. The $-H_{x,y}$ protons of the **C1** appeared at 8.78 ppm and 7.82 ppm as dublets, respectively. In ^{1}H–NMR spectra of the alkylation products of **1**, the $-H_{1,2}$ protons similarly appared around 8.06 ppm to 8.38 ppm region. For its Ru(II) complexes (C**2**-**7**), the $-H_{1,2}$ protons slightly shifted towards upfield region. The ^{1}H-NMR spectra of **C6** and ^{13}C–NMR spectra of **C5** and **C7** have not been monitored due to their low solubility.

The FT-IR spectra recorded with a PerkinElmer FT-IR system are informative, especially for the complexes (C**1**-**7**). For N-bonded thiocyanate complexes (C**1**-**7**), ν_{CN} bands were generally observed around 2093 cm^{-1} to 2104 cm^{-1} region as a strong peak. Additionally, the broad peaks around 3100 cm^{-1} to 3300 cm^{-1} at FT-IR spectra of the complexes showed that the complexes have a hygroscopic nature. Detailed assignments for NMR and FT-IR were made in the experimental part.

The absorbtion spectra of C**1**-**7** in DMF are given Fig. 2a and Table 1. The smaller band or shoulder at around 450 nm results from metal-to-ligand charge transfer (MLCT, [Ru(dπ) $\rightarrow$ π*]) bands, while the intra-ligand $\pi \rightarrow \pi^*$ transitions occur under 400 nm. It is clearly seen that the alkylic modifications in the **1** cause a slight blue-shift at the maxima of MLCT bands. Additionally, the complexes generally have the highest molar extinction coefficient. The optical band gap, obtained from the absorption spectra taken from the literature [49], ranges between 1.81 eV and 2.08 eV.

The electrochemical properties of **C1**-**7** were investigated with cyclic voltammetry using Fc/Fc^{+} redox couple as a reference (Fig. 2b). The voltammograms of all Ru(II) complexes can be classified as an irreversible oxidation process. The oxidation potentials of the sensitizers are very similar except for **C1**. The energy levels of frontier orbitals were calculated from $E_{HOMO} = -E_{ox} + (-4.8)$ for HOMO and from $E_{LUMO} = E_{HOMO} + E_{bg}$ for LUMO [50, 51]. The results are given in Table 1. As a result, LUMO energy levels of all complexes (**C1-7**) are appropriate for electron injection to the TiO_2 conduction band (Fig. 3) [52, 53].

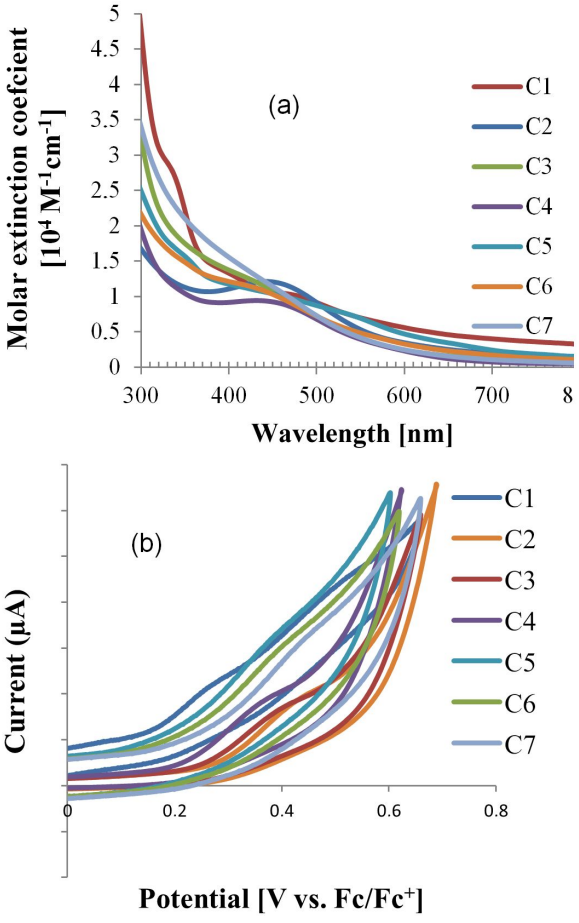

Fig. 2. (a) Absorption spectra of **C1-7** complexes obtained using Thermo Scientific Evolution 201 System. The concentration of all complexes was 1×10^{-5} M in DMF. (b) Cyclic voltammograms of **C1-7** complexes studied in DMF solution (1×10^{-3} M) at a scan rate of 100 m·V·s^{-1}.

The DSSC devices using **C1-7** were prepared using Solaronix 74992 kit. The photoanode was dipped into the **C1-7** solution in DMSO (1 mM) for 24 h at room temperature in the dark. Then, the sandwich-type cells were prepared by assembling with sensitizers coated photoanode and Pt-coated counter electrode. The AN50 electrolyte solution was injected into the pre-drilled hole and sealed using a sealant. The photovoltaic paramaters of DSSCs were monitored using a MTI–BST8–STAT–EIS–LD potentiostat/galvanostat and Abet

Table 1. Optical and electrochemical properties of C1-7.

Compound	λ/nm [$\Sigma/10^4 \cdot M^{-1} \cdot cm^{-1}$]	E^*_{bg} [eV]	E^b_{HOMO} [eV]	E^c_{LUMO} [eV]
C1	475 (1.02)$_{[Ru(d\pi)\rightarrow\pi*]}$; 335 (2.79)$_{\pi\rightarrow\pi*}$	1.99	–5.06	–3.07
C2	442 (1.21)$_{[Ru(d\pi)\rightarrow\pi*]}$; 269 (2.20)$_{\pi\rightarrow\pi*}$	2.04	–5.18	–3.14
C3	442 (1.14)$_{[Ru(d\pi)\rightarrow\pi*]}$; 270 (5.00)$_{\pi\rightarrow\pi*}$	2.08	–5.17	–3.09
C4	432 (0.94)$_{[Ru(d\pi)\rightarrow\pi*]}$; 275 (2.95)$_{\pi\rightarrow\pi*}$	1.81	–5.17	–3.36
C5	461 (1.01)$_{[Ru(d\pi)\rightarrow\pi*]}$; 279 (3.05)$_{\pi\rightarrow\pi*}$	1.85	–5.17	–3.32
C6	443 (1.07)$_{[Ru(d\pi)\rightarrow\pi*]}$; 271 (2.98)$_{\pi\rightarrow\pi*}$	2.00	–5.18	–3.18
C7	462 (1.05)$_{[Ru(d\pi)\rightarrow\pi*]}$; 272 (4.61)$_{\pi\rightarrow\pi*}$	1.97	–5.21	–3.24

*E_{bg} (eV) = 1240/λ_{onset} [49].

Fig. 3. HOMO (–) and LUMO (–) energy levels of the sensitizers together with TiO_2 and I^-/I_3^- levels.

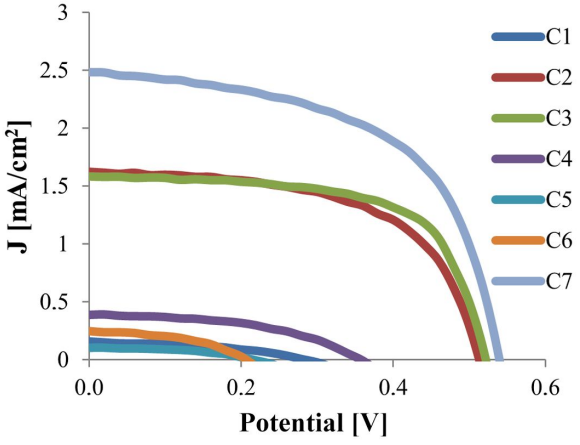

Fig. 4. J-V curves of DSSCs prepared with C1-7.

10500 solar simulator at AM 1.5 condition. The intensity of incoming light was calibrated using a solar-power meter.

The J-V curves of DSSCs prepared with **C1-7** are demonstrated in Fig. 4 under 100 mW·cm^{-2} illumination. Additionally, the photovoltaic performance of **C1-7** under various light intensities are given in Table 2.

The results show that all the compounds are photoactive and may be used as sensitizers in DSSC. Additionally, increasing light intensity generally increases power conversion efficiency of DSSCs (Table 2). The power conversion efficiencies of DSSCs prepared with **C1-7** decrease in the following order: C7 > C3 > C2 > C4 > C6 > C1 under 100 mW·cm^{-2} illumination. But significant efficiencies were obtained from C7, C3, and C2, respectively.

The optimized molecular structures and calculated molecular orbitals of **C1-7** with energy levels under vacuum conditions are demonstrated in Fig. 5.

In **C1-7** complexes, in spite of the fact that LUMO and LUMO+1s are located at the **1-7** ligands, HOMOs and HOMO–1s are largely located at the NCS^- ligands and metal centers. Recently, we have shown that the location of LUMO at anchor ligands directly affects the photoelectron transmission to the TiO_2 conduction band [46]. This phenomenon may be responsible for the moderate activity of **C1-7** as sensitizers in DSSC.

The Gauss-View graphical user interface [53] and Gaussian 03 software package [54] were used for the quantum chemical calculations with the density functional theory. The Becke's three-parameter (B3) nonlocal exchange functional [55] combined with the Lee, Yang, and Parr (LYP) correlation functional [56], denoted as B3LYP, was employed. Ruthenium atom has been represented by the widely used quasi-relativistic

Table 2. Photovoltaic performances of novel sensitizers under various light intensities.

No.	100 mW/cm^2				80 mW/cm^2				60 mW/cm^2				40 mW/cm^2				20 mW/cm^2			
	J_{sc}	V_{oc}	FF	η	J_{sc}	V_{oc}	FF	η	J_{sc}	V_{oc}	FF	η	J_{sc}	V_{oc}	FF	η	J_{sc}	V_{oc}	FF	η
C1	0.159	0.300	0.404	0.019	0.112	0.240	0.454	0.015	0.073	0.240	0.380	0.011	0.05	0.200	0.450	0.011	0.034	0.180	0.362	0.011
C2	1.624	0.520	0.573	0.484	1.076	0.480	0.577	0.372	0.598	0.440	0.571	0.251	.0265	0.380	0.552	0.139	0.084	0.300	0.446	0.056
C3	1.584	0.540	0.619	0.529	1.074	0.500	0.629	0.422	0.615	0.460	0.609	0.287	0.286	0.420	0.587	0.176	0.099	0.360	0.597	0.106
C4	0.389	0.340	0.496	0.066	0.289	0.320	0.492	0.057	0.172	0.280	0.475	0.038	0.093	0.240	0.506	0.028	0.037	0.220	0.659	0.027
C5	0.105	0.220	0.471	0.011	0.086	0.180	0.495	0.009	0.067	0.180	0.394	0.008	0.047	0.160	0.499	0.009	0.042	0.160	0.479	0.016
C6	0.249	0.200	0.460	0.023	0.183	0.180	0.478	0.020	0.116	0.160	0.532	0.016	0.076	0.160	0.416	0.013	0.040	0.140	0.450	0.013
C7	2.484	0.520	0.585	0.756	1.637	0.540	0.538	0.595	0.966	0.520	0.507	0.424	0.440	0.480	0.440	0.232	0.133	0.360	0.417	0.100

V_{oc} is open circuit voltage, J_{sc} is short circuit current, FF (fill factor) = $(J_{max.}V_{max.})/(J_{sc}V_{oc})$, η (power conversion efficiency of DSSC) = $(V_{oc}J_{sc}FF)/(P_oA)$, where P_0 is the applied illumination intensity and A is photoactive area.

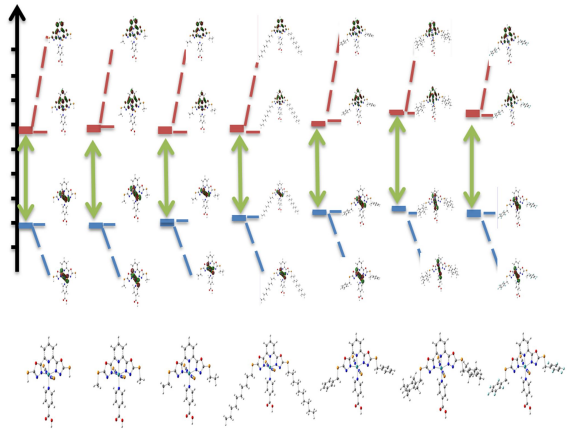

Fig. 5. Optimal molecular structure and isodensity surface plots of HOMOs and LUMOs with enery levels for C1-7 complexes.

LANL2DZ basis set (Los Alamos effective core pseudo-potential plus double-ζ) [57–59], while 6-311G(d,p) basis set [60, 61] has been assigned to the remaining atoms.

4. Conclusions

In this work, we synthesized new Ru(II) complexes (**C1-7**), containing tridentate 5-[6-(5-mercapto-1,3,4-oxadiazol-2-yl)pyridin-2-yl]-1,3,4-oxadiazole-2-thiol's as ancillary ligands and isonicotonic acid as anchor ligands. The photovoltaic parameters of DSSC prepared with the complexes show that the modification of ligands clearly affects DSSC yield. The DSSC using the **C7** complex bearing pentafluorobenzyl groups has a highest power conversion efficiency of 0.76 %. An appropriate optimization may increase power conversion efficiency.

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References

[1] SUN J., REN S.-Z., LU X.-Y., LI J.-J., SHEN F.-Q., XU C., ZHU H.-L., *Bioorgan. Med. Chem.*, 25 (2017) 2593.

[2] GHOZLAN S.A.S., AL-OMAR M.A., AMR A.E.G.E., ALI K.A., EL-WAHAB A.A.A., *J. Heterocyclic Chem.*, 48 (2011) 1103.

[3] MANOJKUMAR P., RAVI T.K., SUBBUCHETTIAR G., *Acta Pharmaceut.*, 59 (2009) 159.

[4] GUDASI K., PATIL M., VADAVI R., SHENOY R., PATIL S., *J. Serb. Chem. Soc.*, 72 (2007) 357.

[5] SEDDON K.R., *Coordin. Chem. Rev.*, 41 (1982) 79.

[6] TRNKA T.M., GRUBBS R.H., *Accounts Chem. Res.*, 34 (2001) 18.

[7] AROCKIAM P.B., BRUNEAU C., DIXNEUF P.H., *Chem. Rev.*, 112 (2012) 5879.

[8] GARBER S.B., KINGSBURY J.S., GRAY B.L., HOVEYDA A.H., *J. Am. Chem. Soc.*, 122 (2000) 8168.

[9] BRUIJNINCX P.C.A., SADLER P.J., *Curr. Opin. Chem. Biol.*, 12 (2008) 197.

[10] ZHANG C.X., LIPPARD S.J., *Curr. Opin. Chem. Biol.*, 7 (2003) 481.

[11] MERCS L., ALBRECHT M., *Chem. Soc. Rev.*, 39 (2010) 1903.

[12] ALESSIO E., MESTRONI G., BERGAMO A., SAVA G., *Curr. Top. Med. Chem.*, 4 (2004) 1525.

[13] ALLARDYCE C.S., DYSON P.J., *Platin. Met. Rev.*, 45 (2001) 62.

[14] SCHMIDT-MENDE L., ZAKEERUDDIN S.M., GRATZEL M., *Appl. Phys. Lett.*, 86 (2005).

[15] SCHMIDT-MENDE L., KROEZE J.E., DURRANT J.R., NAZEERUDDIN M.K., GRATZEL M., *Nano Lett.*, 5 (2005) 1315.

[16] KINOSHITA T., DY J.T., UCHIDA S., KUBO T., SEGAWA H., *Nat. Photonics*, 7 (2013) 535.

[17] DUPREZ V., BIANCARDO M., SPANGGAARD H., KREBS F.C., *Macromolecules*, 38 (2005) 10436.

[18] DAYAN S., KAYACI N., KALAYCIOGLU N.O., DAYAN O., OZTURK E.C., *Inorg. Chim. Acta*, 401 (2013) 107.

[19] CETIN A., DAYAN O., *Chinese J. Chem.*, 27 (2009) 978.

[20] OTER O., ERTEKIN K., DAYAN O., CETINKAYA B., *J. Fluoresc.*, 18 (2008) 269.

[21] DOGAN F., DAYAN O., YUREKLI M., CETINKAYA B., *J. Therm. Anal. Calorim.*, 91 (2008) 943.

[22] SINN S., SCHULZE B., FRIEBE C., BROWN D.G., JÄGER M., ALTUNTAŞ E., KÜBEL J., GUNTNER O., BERLINGUETTE C.P., DIETZEK B., SCHUBERT U.S., *Inorg. Chem.*, 53 (2014) 2083.

[23] LI C.-Y., SU C., WANG H.-H., KUMARESAN P., HSU C.-H., LEE I.T., CHANG W.-C., TINGARE Y.S., LI T.-Y., LIN C.-F., LI W.-R., *Dyes Pigments*, 100 (2014) 57.

[24] SEKAR N., GEHLOT V.Y., *Resonance*, 15 (2010) 819.

[25] AGHAZADA S., GAO P., YELLA A., MAROTTA G., MOEHL T., TEUSCHER J., MOSER J.-E., DE ANGELIS F., GRÄTZEL M., NAZEERUDDIN M.K., *Inorg. Chem.*, 55 (2016) 6653.

[26] PERIS E., CRABTREE R.H., *Coordin Chem Rev*, 248 (2004) 2239.

[27] YI H.N., CRAYSTON J.A., IRVINE J.T.S., *Dalton T.*, (2003) 685.

[28] KUANG D.B., KLEIN C., ITO S., MOSER J.E., HUMPHRY-BAKER R., ZAKEERUDDIN S.M., GRATZEL M., *Adv. Funct. Mater.*, 17 (2007) 154.

[29] NAZEERUDDIN M.K., PÉCHY P., RENOUARD T., ZAKEERUDDIN S.M., HUMPHRY-BAKER R., COMTE P., LISKA P., CEVEY L., COSTA E., SHKLOVER V., SPICCIA L., DEACON G.B., BIGNOZZI C.A., GRÄTZEL M., *J. Am. Chem. Soc.*, 123 (2001) 1613.

[30] KOOPS S.E., O'REGAN B.C., BARNES P.R.F., DURRANT J.R., *J. Am. Chem. Soc.*, 131 (2009) 4808.

[31] TATAROGLU A., OCAYA R., DERE A., DAYAN O., SERBETCI Z., AL-SEHEMI A.G., SOYLU M., AL-GHAMDI A.A., YAKUPHANOGLU F., *JJOEM*, 47 (2018) 828.

[32] ELGAZZAR E., DAYAN O., SERBETCI Z., DERE A., AL-SEHEMI A.G., AL-GHAMDI A.A., EL-TANTAWY F., FAROOQ W.A., YAKUPHANOGLU F., *Physica B: Condens. Mater.*, 516 (2017) 7.

[33] TATAROĞLU A., DAYAN O., ÖZDEMIR N., SERBETCI Z., AL-GHAMDI A.A., DERE A., EL-TANTAWY F., YAKUPHANOGLU F., *Dyes Pigments*, 132 (2016) 64.

[34] SOYLU M., ORAK I., DAYAN O., SERBETCI Z., *Microelectron. Reliab.*, 55 (2015) 2685.

[35] OREGAN B., GRATZEL M., *Nature*, 353 (1991) 737.

[36] HAGFELDT A., BOSCHLOO G., SUN L., KLOO L., PETTERSSON H., *Chem. Rev.*, 110 (2010) 6595.

[37] GRÄTZEL M., *J. Photochem. Photobiol. C: Photochem. Rev.*, 4 (2003) 145.

[38] MATHEW S., YELLA A., GAO P., HUMPHRY-BAKER R., CURCHOD B.F.E., ASHARI-ASTANI N., TAVERNELLI I., ROTHLISBERGER U., NAZEERUDDIN M.K., GRATZEL M., *Nat. Chem.*, 6 (2014) 242.

[39] AMARESH M., R. F.M.K., PETER B., *Angew. Chem. Int. Ed.*, 48 (2009) 2474.

[40] GAO F., WANG Y., SHI D., ZHANG J., WANG M., JING X., HUMPHRY-BAKER R., WANG P., ZAKEERUDDIN S.M., GRÄTZEL M., *J. Am. Chem. Soc.*, 130 (2008) 10720.

[41] HORIUCHI T., MIURA H., SUMIOKA K., UCHIDA S., *J. Am. Chem. Soc.*, 126 (2004) 12218.

[42] CHEN C.-Y., WANG M., LI J.-Y., POOTRAKULCHOTE N., ALIBABAEI L., NGOC-LE C.-H., DECOPPET J.-D., TSAI J.-H., GRÄTZEL C., WU C.-G., ZAKEERUDDIN S.M., GRÄTZEL M., *ACS Nano*, 3 (2009) 3103.

[43] KONTI G., CHATZIVASILOGLOU E., LIKODIMOS V., KANTONIS G., KONTOS A.G., PHILIPPOPOULOS A.I., FALARAS P., *Photochem. Photobiol. Sci.*, 8 (2009) 726.

[44] BREWSTER T.P., KONEZNY S.J., SHEEHAN S.W., MARTINI L.A., SCHMUTTENMAER C.A., BATISTA V.S., CRABTREE R.H., *Inorg. Chem.*, 52 (2013) 6752.

[45] GAJARDO F., LEIVA A.M., LOEB B., DELGADILLO A., STROMBERG J.R., MEYER G.J., *Inorg. Chim. Acta*, 361 (2008) 613.

[46] DAYAN O., OZDEMIR N., YAKUPHANOGLU F., SERBETCI Z., BILICI A., CETINKAYA B., TERCAN M., *J. Mater. Sci.-Mater. El.*, 29 (2018) 11045.

[47] GONG J., LIANG J., SUMATHY K., *Renew. Sustain. Energ. Rev.*, 16 (2012) 5848.

[48] ZHENG Q.Z., ZHANG X.M., XU Y., CHENG K., JIAO Q.C., ZHU H.L., *Bioorgan. Med. Chem.*, 18 (2010) 7836.

[49] COLLADET K., NICOLAS M., GORIS L., LUTSEN L., VANDERZANDE D., *Thin Solid Films*, 451 (2004) 7.

[50] CHEN B., LI Y.H., YANG W., LUO W., WU H.B., *Org. Electron.*, 12 (2011) 766.

[51] LU Z.Z., PENG J.D., WU A.K., LIN C.H., WU C.G., HO K.C., LIN Y.C., LU K.L., *Eur. J. Inorg. Chem.*, (2016) 1214.

[52] KATOH R., FURUBE A., *J. Photoch. Photobio. C*, 20 (2014) 1.

[53] DENNINGTON R., KEITH T., MILLAM J.G., *Semichem. Inc.*, (2007).

[54] TRUCKS G., SCHLEGEL H., SCUSERIA G., ROBB M., CHEESEMAN J., MONTGOMERY JR J., VREVEN T., KUDIN K., BURANT J., MILLAM J., *Gaussian Inc., Wallingford, CT*, (2004).

[55] BECKE A.D., *J. Chem. Phys*, 98 (1993) 5648.

[56] LEE C., YANG W., PARR R.G., *Phys. Rev. B*, 37 (1988) 785.

[57] HAY P.J., WADT W.R., *J. Chem. Phys.*, 82 (1985) 270.

[58] WADT W.R., HAY P.J., *J. Chem. Phys.*, 82 (1985) 284.
[59] HAY P.J., WADT W.R., *J. Chem. Phys.*, 82 (1985) 299.
[60] MCLEAN A., CHANDLER G., *J. Chem. Phys.*, 72 (1980) 5639.
[61] KRISHNAN R., BINKLEY J.S., SEEGER R., POPLE J.A., *J. Chem. Phys.*, 72 (1980) 650.

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