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A ruthenium tetrazole complex-based high efficiency

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We report on the exploitation of a new tetrazole-substituted 1,10phenanthroline and a 2,2'-bipyridine (bpy) ancillary ligand modified by an electron-donating group in cationic ruthenium complexes. This complex, placed in between two electrodes without any polymer, demonstrates high efficiency near-infrared (NIR) electroluminescence (EL). The comparison between bpy and its methyl-substituted ancillary ligand shows that the cationic Ru tetrazolate complex containing methyl groups exhibits a red shift in EL wavelength from 620 to 800 nm compared to $[Ru(bpy)_3]^{2+}$ and an almost twofold reduction of turn-on voltage, *i.e.*, from 5 to 3 V, with respect to 5-tetrazole-1,10-phenanthroline. We achieved an external quantum efficiency value of 0.95% for the dimethyl derivative, which is a remarkable result for non-doped NIR light electrochemical cells based on ruthenium polypyridyl.

A major challenge for scientists designing new generations of light emitting diodes (LEDs) is finding novel materials that combine important aspects such as environmental friendliness, high efficiency and economical cost. 1,2 Solid-state lighting (SSL) classes, including light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs), often reliably possess all the above requirements.³ Among SSLs, light electrochemical cells (LECs) are the simplest LED class, which provide some exclusive properties not found in other classes. Some remarkable advantages of LECs compared to OLEDs include the following: (i) their figures of merit do not strongly depend on the thickness of the layers, (ii) the difference of the work functions of the electrodes does not affect the external quantum efficiency (EQE), (iii) the value of the turn-on voltage is close to the optical band gap of the light-emitting layer, and (iv) LECs have a simple and inexpensive architecture due to the reduction of the number of deposited layers.⁴ However, the optimization of the emitter layer is not trivial and has several issues. The alignment of the HOMO and LUMO of the complex

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with the energy level of anode and cathode electrodes and the charge transport process remain issues to be solved to enhance the LEC performances.⁵ Ruthenium(II) polypyridyl complexes are suitable candidates for the light-emitting layer;6 as they are in high demand, they are currently less expensive than iridium cyclometalated complexes.7 However, most ruthenium-based LECs emit in the orange and red spectral regions.⁸ To overcome this limitation and tune the emission wavelength, a main strategy is the substitution of different functional groups including electron donor-acceptors on πconjugated ligands.⁹ Near-infrared (NIR) light-emitting sources are typically expensive due to the exploitation of multi layers costly material. 7 In this context, LECs could serve as low-cost alternatives in application areas where NIR luminescence has a key role such as telecommunications,¹⁰ bio-imaging¹¹ and wound healing.^{9,12} However, solid-state NIR LECs, *i.e.*, having the EL peak wavelength in the NIR, are not fully investigated, being the research effort mostly focused on ionic transitionmetal complexes (iTMCs).³ The intrinsic difficulty of NIR-EL emission arises from the energy gap law that disfavors radiative transition at lower emission energies, which causes these systems to exhibit EQEs <0.1%.6a,13 Intensive research has been focused on modifying ligands coordination sphere to induce a red shift in emission wavelength and to improve the overall efficiency of NIR EL. Moreover, since the design of ligands around the metal cores is key in the electron transfer process and light-emitting performances,14 the introduction of aromatic rings, containing multi nitrogen donor atoms such imydazolyl,15 triazolyl 16 or pyrazolyl 17 rings in the backbone of polypyridyl ligand, allowed the modulation of the spectroscopic and redox properties through the tuning of the HOMO and LUMO gap of the resulting complexes.¹⁸ However, literature on the incorporation of tetrazole ring on polypyridyl ligand is not exhaustive to date. Here, we propose new NIR electroluminescent compounds, investigating the effect of ancillary ligands. For this purpose, we designed and synthesized a series of novel ruthenium(II) complexes containing 5-tetrazole-1,10-phenanthroline (Tzphen) and 2,2'bipyridine (bpy), 4,4'-di-methyl-2,2'-bipyridine (dmbpy), or 1,10-phenanthroline (phen) as ancillary ligands, named as SA1-SA3. The schematic of the synthesis procedure and the structures of the ligands and their complexes [Ru(Tzphen)(N N)2](ClO4)2, SA1-SA3,

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Table 1. UV/Vis, PL and redox properties of SA1-SA3.^aInDMF solutions (1×10^{-5} M). ^bIn degassed DMF solutions at 298 K. ^c From CV measurements, $E_{1/2}=1/2(Ep_a+E_{pc})$; 0.1 M acetonitrile/TBAP versus Ag/AgCl. ^d $E_{HOMO}=-(E_{ox}(vs.F_c/F_C^+)+4.8 \text{ eV})$, $E_{LUMO}=E_{HOMO}+E_{0.0} \text{ eV}$, $E_{0.0}$ was calculated from the intersection of absorption and emission spectra in acetonitrile solution.

| Complexes | Absorbance λ (ε) ª | Emission λ _{max} (Φ) ^b | E _{ox} (V) ^c | E _{red} 1/2 (V) ^c | HOMOd | LUMO ^e | E ₀₋₀ f (eV) |
|------------|-----------------------|---|----------------------------------|---------------------------------------|-------|-------------------|-------------------------|
| SA1 | 447 (3.55) | 629(0.055) | +1.34 | -1.31, -1.52 | -6.15 | - 3.89 | 2.26 |
| SA2 | 460 (3.75) | 659(0.067) | +1.28 | -1.13, -1.51 | -6.16 | - 3.97 | 2.19 |
| SA3 | 456 (3.90) | 618(0.012) | 1.36 | -1.30, -1.45 | -6.08 | - 3.79 | 2.29 |
| Ru(bpy)₃²+ | 451 (4.17) | 621 (0.095) | 1.29 i | -1.31i | -5.74 | - 3.14 | 2.60 |

are shown in Fig. 1 (see Supplementary Information –ESI-for the synthesis details and the characterization). The structures of the complexes are identified by FTIR spectroscopy, all displaying the characteristic band of the N-H of Tzphen at 2950 cm⁻¹. Moreover, the removal of the CN band at 2200 cm⁻¹ in phen(CN) indicates the formation of the Tzphen ligand.²⁰ Analyzing the ¹H NMR spectra, for all complexes, it is possible to observe the signals at approximately 8.8 ppm associated with the CH of C6 in the Tzphen ligand (ESI.S2, Figs. S1, S3, S5). The ¹³C NMR spectra of SA1-3 show the tetrazole carbon (Ct) resonance (*i.e.*, chemical-shift value $\delta \approx 162$ ppm) ²¹ (see ESI S2, Figs S2, S4 and S6), a clear evidence of the presence of tetrazole moiety in the complexes.



Figure 1..a) Chemical structures of Tzphen ligand and SA1-SA3 complexes The synthesis procedure is summarized: (i) NaClO, tetrabutyl ammonium hydrogen sulfate (TBAHS), pH=8.5, 18 °C, 2h (ii) KCN, H₂O, 4h (iii) NaN₃, NH₄Cl, DMF, 140 °C, 48h (iv) H₂O,HCl, pH=3.5 (v) RuCl₃.xH₂O, 2mol N^N, 5 h reflux in DMF, 140°C (vi) Tzphen, 5 h reflux, 140°C.

Characterizations by elemental analysis and electrospray ionization mass spectrometry (ESI-mass) also confirm the synthesis of the complexes. Specific data are given in the Supplementary Information. The UV–Vis absorption and photoluminescence (PL) spectra of the complexes in N, N dimethyl formamide (DMF) solutions are shown in Figure 2 and summarized in Table 1. Complexes SA1–SA3 show intense intra-ligand absorption bands in the UV region and less intense metal-to-ligand charge-transfer (MLCT) absorption bands at ≈450nm with a tail extending up to 530 nm.²² The latter bands are originated from excitation of an electron from the ruthenium-based t_{2g} HOMO to the low-lying unoccupied π^* anti-bonding orbital of the ligands. This is confirmed by time dependent density functional theory (TDDFT) calculations, see ESI, S3, Table S2. Calculations predict a spin-orbit coupling on the lowest energy band of prototype SA1 complex, leading to broadening and red-shifting of the lowest absorption band, with the appearance of the band tail, which is experimentally observed, see ESI.S3, Fig S8-S11. The $\lambda_{\text{max,abs}}$ of the MLCT values in the series follow the expected trend of increasing electron donation, following the sequence SA3 <SA1<SA2. The room temperature photoluminescence (PL) emission spectra of the complexes display a broad and featureless band in DMF solution, and the emission spectrum of complex SA2 is red shifted by approximately 40 nm compared to SA1. According to DFT calculation, this result also demonstrates that the presence of the electron-donating methyl groups on the dmbpy ligands of complex SA2 destabilizes the HOMO of complex SA2 compared to complexes SA1 and SA3 (ESI. S7 and S8).



Figure 2. UV-Visible region of absorption and PL (λ_{exc} =405 nm) spectra of Ru(Tzphen) complexes (SA1-SA3) in DMF solution at 10⁻⁵ M. The star shows the second harmonic of laser radiation.

To determine the LEC performance of the as-synthesized emitters, it is key to investigate the oxidation-reduction properties. In this context, the electrochemical behaviours of SA1-SA3 were investigated by cyclic voltammetry (CV) (Figure 3). The nature of the ancillary ligands affects both the potentials and the quasi-reversibility of the redox processes. All compounds display one oxidation half-wave in the positive region due to the oxidation/reduction (Ox/Red) of Ru(II) to Ru(III) and three reduction processes in the negative potential region due to the Ox/Red of the ligands. The inset of Figure 3 also shows the oxidation wave of SA2 on the platinum electrode at various scan rates ranging from 0.00 to 300 mV s⁻¹. Moreover, there is a linear correlation between the anodic current and u1/2, suggesting that the kinetics of the overall process is controlled by mass transport. The formal half-wave potential values of the quasi-reversible processes are reported in Table 1.

Table 2. Electroluminescence Spectral Data of $ITO/[Ru(N^N)_2(Tzphen)]^{2+}$ / Ga:In Devices.^aCIE(x, y): Commission Internationale de L'Eclairage.^b Maximum current density (mA cm⁻²).Turn-on voltage (V).^c Maximum luminance, L_{max}, (cd m⁻²). ^d Luminous efficiency, L_{eff}, (cdA⁻¹) ^e External quantum efficiency (%) at 6 V.

| Complexes | λ_{max} | CIE ^a | FWHM | J_{max}^b | V turn on | L _{max} c | Leff ^d [cd A ⁻¹] | EQE ^e (%) |
|------------|-----------------|------------------|------|------------------------|-----------|-----------------------|---|----------------------|
| | (EL)[nm] | [x, y] | [nm] | [mA cm ⁻²] | [V] | [cd m ⁻²] | | |
| SA1 | 690 | [0.652,0.315] | 155 | 450 at 6 (V) | 5.0 | 375 at 6 (V) | 0.85 at 6 (V) | 0.55 |
| SA2 | 725, 800 | [0.662, 0.316] | 153 | 475 at 4 (V) | 3.0 | 360 at 4 (V) | 0.75 at 4 (V) | 0.95 |
| Ru(bpy)₃²+ | 632 | [0.693, 0.308] | 137 | 185 at 4(V) | 2.3 | 1800 at 4 (V) | - | 1.2 |



Figure 3. Cyclic voltammograms of complexes SA1-SA3 acetonitrile solution under N_2 atmosphere. Inset: Cyclic voltammograms of SA2 on platinum electrode at various scan rates; (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, and (f) 300 mV s⁻¹

It is useful to note the cyclic voltammetry of SA1-3 is very sensitive to the nature of solvent which the polarity of solvent will effect on the redox behaviour.²³ All three complexes in DMF solvent were shown irreversible redox properties However, as shown in figure 3, the CV of SA1-3 in acetonitrile solvent was shown quasi-reversible half-wave potentials.

The electronic nature of the dmbpy ligand (R =CH₃) influences the π^* acceptor energy levels in SA2. The introducing electrondonating methyl groups destabilize the bpy- π^* orbitals, decreasing the extent of $d_{\pi^{-}\pi^{*}}$ back-bonding from Ru(II) to the dmbpy ligand. This decreased back-bonding destabilizes the d_{π^6} core, diminishing the Ru^{3+/2+} redox potentials with respect to SA1, which is containing bpy ancillary ligand. This result suggests a low turn-on voltage due to the low driving force for ion mobility in a LEC. In the following, we describe a simple LEC formed by the [Ru(N^N)₂(Tzphen)] complex and two electrodes, i.e., without PEDOT: PSS or any doped-polymeric layers. ²⁴ Moreover, the working devices were obtained using low melting point alloy (Ga:In) cathode contacts, which potentially allows the avoidance of vacuum evaporation techniques. Upon application of a bias < 3V to the ITO/SA2/Ga:In device, light emission and current density dramatically increase over time. However, all our attempts to obtain a suitably compact layer of SA3 failed because of the aggregation of SA3 under the surface. ²⁵ The EL spectra have a broad line shape, which are similar to those of the PL spectra obtained from the complexes in solution, showing only a red shift of ≈100 nm in wavelength maxima (Figure 2). The device based on SA2 shows two broad bands at ≈725 and ≈ 800nm, which are the lowest-energy emissions observed so far in LEC devices based on ruthenium tetrazole complexes.²⁶



Figure 4. EL spectra of Ru SA1 and SA2 and $[Ru(bpy)_3]^{2+}$ as reference. Inset: the photograph of LEC emission based on SA1.

The current over time for the two devices is almost the same and shows good stability (ESI. Fig. S13). Moreover, the LEC based on complex SA2 with substituted bpy has a significantly lower turn-on voltage than SA1 with bpy, at 3 and 5 V, respectively,²⁷ reaching luminance values up 360 cd/m² in the NIR region.



Figure 5. Current density and maximum luminance versus applied voltage for Ru-based LEC devices (SA1 and SA2).

Currently, the highest demonstrated EQE value of NIR EL for a LEC with an anode (ITO)/ Ru polypyridyl complex/cathode (Au) configuration is 0.03%, ²⁸ while the addition of hole-or electron-assisted polymers such as PEDOT: PSS allows to achieve an EQE value of 2.06%. ²⁹ The latter being the current record high for such devices. The EQE value of 0.95% for SA2 represents the current state of the art for a NIR LEC based on the ruthenium polypyridyl family with a configuration of anode(ITO)/Ru polypyridyl complex/cathode (Ga:In) (see ESI Table S3.). ³⁰ The remarkable EL performances, i.e., low turn on

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voltage and high EQE, demonstrate the influence of the electron-donating group in the ancillary ligand.

In conclusion, this manuscript reports the synthesis of novel Ru complexes and their exploitation in NIR LECs, achieving EQE up to 0.95%. The influence of the electron-donating group in tuning the EL wavelength as well as the turn-on voltage of the devices is clearly observed, as the turn-on voltage is reduced from ≈ 5 V to ≈ 3 V with respect to non-dimethyl bpy derivate. The simple design of the proposed device is remarkable, avoiding the use of PEDOT: PSS or other hole-electron transport layer. In addition, the possibility to use liquid Ga:In cathode is particular interesting for the commercial application such as printing and injection methods for cathode deposition.

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■REFERENCES

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1. Gustavsson, S. B., The Nobel Prize in Physics 2014 , The Royal Swedish Academy of Sciences, 2014 http://www. nobelprize.org/ nobel_prizes/ physics/ laureates/.

2. Zheludev, N. Nature Photonics. 2007,1, 189.

3. Costa, R. D.; Ortí, E.; Bolink, H. J.; Monti, F.; Accorsi, G.; Armaroli, N., Angew. Chem. Int. Ed. **2012**, 51, 8178.

4.(a) Buda, M.; Kalyuzhny, G.; Bard, A. J. *J. Am. Chem. Soc.* **2002**, 124, 6090; (b) Kalyuzhny, G.; Buda, M.; McNeill, J.; Barbara, P.; Bard, A. J. s, *J. Am. Chem. Soc.* **2003**, 125, 6272. (c) R- D. Costa.; E. Ortí.; H- J. Bolink.; S, Graber.; C- E, Housecroft.; M, Neuburger.; S, Schaffner.; E- C. Constable, *Chem. Commun.*, **2009**, 2029. 5. (a) Bolink, H. J.; Cappelli, L.; Coronado, E.; Gavina, P. *Inorg. chem.* **2005**, 44, 5966; (b) Tsai, C.-S.; Yang, S.-H.; Liu, B.-C.; Su, H.-C., *Org. Elec.* **2013**, 14, 488.

6.(a) Tordera, D.; Frey, J.; Vonlanthen, D.; Constable, E.; Pertegás, A.; Ortí, E.; Bolink, H. J.; Baranoff, E.; Nazeeruddin, M. K., *Adv. Eunc. Mater.2013*,3, 1338;(b) Tordera, D.; Meier, S.; Lenes, M.; Costa, R. D.; Ortí, E.; Sarfert, W.; Bolink, H. J. *Adv. Mater.*, **2012**, 24, 897.

7.Edited book by Hartmut Yersinen title "Highly efficient O leds with phosphorescent materials ", 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Chapter 5, page 203.

8. Slinker, J.; Bernards, D.; Houston, P. L.; Abruña, H. D.; Bernhard, S.; Malliaras, G. G., *Chem. Commun.* **2003**, 2392.

9. Rausch, A. F.; Thompson, M. E.; Yersin, H., J. Phys. Chem. A. 2009, 113, 5927.

10 (a) N. Tessler, V. Medvedev, M. Kazes, S. H. Kan, and U. Banin, *Science* **2002**, 295, 1506, (b) L. H. Slooff, A. Polman, F. Cacialli, R. H. Friend, G. A. Hebbink, F. van Veggel, D. N. Reinhoudt, *Appl. Phys. Lett.* **2001**, 78, 2122. (c) R. J. Curry, W. P. Gillin, *Appl. Phys. Lett.* **1999**, 75, 1380.

11. (a) S. A. Priola, A. Raines, W. S. Caughey, *Science* **2000**, 287, 1503. (b) . H. T. Whelan, R. L. Smits, E. V. Buchman, N. T. Whelan, S. G. Turner, D. A. Margolis, V. Cevenini, H. Stinson, R. Ignatius, T. Martin, J. Cwiklinski, A. F. Philippi, W. R. Graf, B. Hodgson, L. Gould, M. Kane, G. Chen, and J. Caviness, J. Clin. Laser Med. Sur. **2001**, 19, 305. (b) T. Karu, The Science of Low-Power Laser Theraphy (Gordon and Breach Scientific, New York, 1998. (c) R. Raghavachari, Near-Infrared Applications in Biotechnology ,CRC, Boca Raton, 2001. (d) E. Desurvire, Erbium-Doped Fiber Amplifiers: Principles and Applications, WileyInterscience, New York, 1994.

12. Bünzli, J.-C. G.; Eliseeva, S. V., J Rare Earth. 2010, 28, 824.

13. (a) Bolink, H. J.; Coronado, E.; Costa, R. D.; Gavina, P.; Ortí, E.; Tatay, S. *Inorg. chem.* **2009**, 48, 3907; (b) Hosseini, A. R.; Koh, C. Y.; Slinker, J. D.; Flores-Torres, S.; Abruña, H. D.; Malliaras, G. G. *Chem. Mater.* **2005**, *17*, 6114.(c) M. Pope , C. E. Swenberg, Electronic Processes in Organic Crystals and Polymers, 2nd ed. (Oxford University Press, New York, 1999).

14. (a) Balzani, V.; Juris, A. *Coord. Chem. Rev.* **2001**, 211, 97. (b) Vos, J. G.; Kelly, J. M. *Dalton Trans*. **2006**, 4869.

15. (a) M. J. Han, L. H. Gao, Y. Y. Lu, K. Z. Wang, *J. Phys. Chem. B* **2006**, 110, 2364; (b) M.-A.Haga, T. Takasugi, A. Tomie, M. Ishizuya, T. Yamada, M. D. Hossain, M. Inoue, *Dalton Trans*. **2003**, 2069

16. (a) W. R. Browne, R. Hage, J. G. Vos, *Coord. Chem. Rev.* 2006, 250, 1653.
(b) M. H. Klingele, S. Brooker, *Coord. Chem. Rev.* 2003, 241, 119. (c) S. Fanni,
T. E. Keyes, C. M. O'Connor, H. Hughes, R. Wang, J. G. Vos, *Coord. Chem. Rev.* 2000, 208, 77.

17. N. Chanda, B. Sarkar, S. Kar, J. Fiedler, W. Kaim, G. K. Lahiri, *Inorg. Chem.* 2004, 43, 5128. (b) C. Sens, M. Rodriguez, I. Romero, A. Llobet, T. Parella, J. Benet-Buchholz, *Inorg. Chem.* 2003, 42, 8385. (c) R. H. Laye, S. M. Couchman, M. D. Ward, *Inorg. Chem.* 2001, 40, 4089.

18. L.-L. Wu, C.-H. Yang, I.-W. Sun, S.-Y. Chu, P.-C. Kao, H.-H. Huang, Organometallics 2007, 26, 2017.

19.W. Zhang, F. Zhao, T. Liu, M. Yuan, Z-M Wang, S. Gao, *Inorg. Chem.* **2007**, 46, 2541.

20.(a) F. Himo, Z. P. Demko, L. Noodleman, K. B. Sharpless, *J. Am. Chem. Soc.*, **2002**, 124, 12210. (b) M. Alterman, A. Hallberg, *J. Org. Chem.*, **2000**, 65, 7984. (c) F. Himo, Z. P. Demko, L. Noodleman, K. B Sharpless, *J. Am. Chem. Soc.*, **2003**, 125, 9983. (d) D. P. Matthews, J. E. Green, A. J. Shuker. *J. Comb. Chem.*, **2000**, 2, 19.

21. (a) S, Stagni.; E, Orselli.; A, Palazzi.; L, De Cola.; S, Zacchini.; C, Femoni.; M, Marcaccio.; F, Paolucci.; S, Zanarini, *Inorg. Chem.* **2007**, 46, 9126.S, (b) Zanarini.; A J. Bard.; M, Marcaccio.; A, Palazzi.; F, Paolucci.; S, Stagni.; *J. Phys. Chem. B* **2006**, 110, 22551.

22. D. L. Ashford, C.r R. K. Glasson, M.R. Norris, J. J. Concepcion, S. Keinan, M. K. Brennaman, J. L. Templeton, T. J. Meyer , *Inorg. Chem.* 2014, 53 (11), 5637 . (b) P.A. Anderson, G.F. Strouse, J.A. Treadway, F.R. Keene, T.J. Meyer, *Inorg. Chem.* 1994, 33, 3863, (c) W.V. Yam, W.V. Lee, K.M. Siu, , *Inorg. Chem.* 1997, 36, 2124, (d) B. Gholamkhass, K. Koike, N. Negishi, H. Hori and K. Takeuchi, *Inorg. Chem.*, 2001, 40, 756, (e) D. P. Rillema, D. G. Taghdiri, D. S. Jones, C. D. Keller, L. A. Worl, T. J. Meyer and H. A. Levy, *Inorg. Chem.*, 1987, 26, 578, (f) Bryan A. Albani, Christopher B. Durr, and Claudia Turro, *J. Phys Chem* A 2013, 117 (50), 13885. (g) D. S. Seneviratne, Md. J. Uddin, V. Swayambunathan, H. B. Schlegel, J. F. Endicott, *Inorg. Chem.* 2002, 41 (6), 1502, (h) S. Bodige, A. S. Torres, D. J. Maloney, D. Tate, G. R. Kinsel, J. K. Walker and F. M. MacDonnell, *J. Am. Chem. Soc.*, 1997, 119, 10364.

23. P. Zanello, Inorganic Electrochemistry, Theory, Practice and Application, The Royal Society of Chemistry 2003.

24.. (a) Gao, F. G.; Bard, A. J., *Chem. Mater.* **2002**, 14, 3465. (b) Tokel, N. E.; Bard, A. J., *J. Am. Chem. Soc.* **1972**, 94, 2862.

25. Dreyse, P.; Loe,B.; Soto-Arriaza, M.; Tordera, D.; Ortí, E.; Serrano-Pérez, J.; Bolink, H. J, *Dalton Trans*, **2013**, 42, 15502.

26. (a) Shahroosvand, H.; Najafi, L.; Sousaraei, A.; Mohajerani, E.; Janghouri, M.; Bonaccorso, F.; *J. Phys. Chem. C*, **2016**, 120, 24965. (b) Stagni, S.; Palazzi, A.; Zacchini, S.; Ballarin, B.; Bruno, C.; Marcaccio, M.; Paolucci, F.; Monari, M.; Carano, M.; Bard, A. *Inorg. Chem.* **2006**, 45, 695. (c) Shahroosvand, H.; Najafi, L.; Sousaraei, A.; Mohajerani, E.; Janghouri, M.J. Mater. Chem. C, **2013**, 1, 6970. (d) Shahroosvand, H.; Najafi, L.; Mohajerani, E.; Janghouri, M.; Nasrollahzadeh, M. *RSC Adv.* **2013**, 3, 6323.

27. (a) Note: people can see infrared up to at least 1050 nm in experiments. (b) D-H, Sliney.;R-T, Wangemann.; J- K, Franks,.; M-L. Wolbarsht, *J Opt. Soc. Amer.* **1976**, 66 (4), 339.(c) D- K, Lynch.; ,W- C, Livingston, Color and Light in Nature (2nd ed.). Cambridge, UK: Cambridge University Press. 2001, .p. 231. ISBN 978-0-521-77504-5. (d), M- C, Dash.; P,Satya, Limits of the eye's overall range of sensitivity extends from about 310 to 1050 nanometersFundamentals 0f Ecology 3E. Tata McGraw-Hill Education. 2009, p. 213. ISBN 978-1-259-08109-5.
28. S,Xun.; J. Zhang.; X. Li.; D, Ma.; Z, Yuan Wang, *Syn. Met.* **2008**, 158, 484.

29. J-H, Hsu.; H-C, Su.; Phys. Chem. Chem. Phys., 2016, 18, 5034.

 A, Breivogel.; M, Park.; D, Lee,S, Klassen.; A, Kühnle.; C, Lee.; K, Char.; K, Heinze, *Eur. J. Inorg. Chem.* **2014**, 288. H, Bolink.; E, Coronado.; R, Costa.; P, Gavina.; E, Ortí.; S, Tatay, *Inorg. Chem.* **2009**, 48, 3907.