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TD-DFT study of charge transfer excitation in D- π -A metal complex dyes as sensitizers in DSSCs

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ABSTRACT

The intra-molecular charge transfer electronic transition in a series of D- π -A metal complexes dyes which could be used as sensitizers in DSSCs have been studied utilizing the TD-DFT method. The structure of these dyes are shown in figure 1, where different π -spacers (S) namely; benzene, furan, pyrrole and thiophene have been assigned. The transition metals studied were Co(III), Ni(II), Cu(I) and Zn(II) and the acceptor part in the dye was taken as 2-cyanoacrylic acid. The geometrical and electronic spectral properties of these dyes were calculated at the PBE/6-31G level of theory in order to understand the mechanism of the intra-molecular charge transfer electronic transition taking place in these systems. It is found that the amount of charge transferred on going from the ground state to the excited state (q^{cT}) depend on the type of the metal as well as the π -linker used. For all the π -spacers (S) the amount of q^{cT} was found to increase in the order Co(III) < Ni(II) < Cu(I) < Zn(II) metal complex dyes. For Co(III) and Cu(I) complexes the thiophene π -spacer was found to be the best in enhancing the CT process while the largest calculated value of q^{cT} for Ni(II) and Zn(II) complexes was found with the pyrrole moiety as the π -spacer. Calculated descriptors of the charge transfer transition for all the studied dyes have been reported and discussed.

Keywords: DSSCs, Thiophene-π-spacers, Light harvesting efficiency, TD-DFT, BPE

INTRODUTION

Molecular modeling through structural modifications of the D- π -A metal as well as metal free dyes, could strongly help in enhancing their efficiency as sensitizers in DSSCs. Metal complexes dyes, in particular Ru-based proved to be the most efficient in solar-to-electrical power conversion. In fact, since the early pioneer work of O'Regan and Gratzel [1-3] using Ru-based dyes as sensitizers in DSSCs, there have been a tremendous growth of experimental as well as theoretical investigations of the sensitization process of several organic and inorganic dyes [4-6]. It has been concluded [4-6] that it is crucial to acquire a complete understanding of the different processes taking place in DSSCs specially the electron transfer phenomena to improve the performance of the photovoltaic devices.

To develop efficient sensitizers for DSSCs with enhanced electron transfer process at the interface of the dye with the nanocrystalline semiconductor such as TiO_2 a large number of experimental as well as theoretical studies have been performed [7- 50] and this research interest has never ceased to grow. The TD-DFT calculations of the different electronic properties of metal and metal free dyes proved to be a reliable tool for understanding geometrical as well as electronic spectral aspects of these dyes as sensitizers in DSSCs [10-19, 35-50].

For dyes of transition metal complexes the metal-to-ligand charge transfer (MLCT) electronic transition gives rise to an intense absorption band in the visible region. This increases the efficiency of solar energy harvesting and in turn potential use of such dyes in DSSCs. The light driven interfacial electron injection process when the transition metal complex dye anchored on nanocrystalline TiO₂ surface has been theoretically described [4-6]. Also, some indexes analyzing the MLCT transition based on the variation of electronic charge densities as a result of electronic excitation were proposed [12-16]. These indexes define the amount of charge transferred upon going from the ground to the excited state and the associated change in molecular dipole moment. In addition , barycenters of the density depletion and the density increment zones associated with the CT electronic transition and the associated CT length have been defined [12,13] and also an index which defines the overlap between the centroids and could be used to test the performance of TD-DFT for the description of through space CT transitions. A discussion of how these indices derived from TD-DFT computed electron density variations could be used to develop either new dyes of metal complexes or new organic dyes for sensitization in DSSCs has been given[14-16].

In the present work, the above mentioned proposed [12,13] indices have been calculated using TD-DFT method for a series of Co(III), Ni(II), Cu(I) and Zn(II) metal complexes dyes having the sequence D- π -A as sensitizers in DSSCs. The general structure of these metal complexes dyes is given in figure 1 where the π -spacer group S is changed from benzene (I) to furan (II), pyrrole (III) and thiophene (IV) to determine the effects of these π -conjugating groups on the efficiency of these metal complexes dyes. The amount of charge transferred and the CT excitation length upon light absorption for each metal complex dye have been calculated utilizing TD-DFT method and the results obtained are reported and discussed.



CALCULATIONS

In the CT model proposed by Bahers, Amado and Ciofini [12,13], the changes in the partial atomic charges (Δq_i) as a result of vertical excitation of the dye molecule from its ground state (GS) to the CT excited state (ES) are defined for each atom (i) whose Cartesian coordinates are (x_i , y_i , and z_i) and calculated as follows:

$$\Delta q_i = q_i^{ES} - q_i^{GS}$$

$$= q_i^+ \text{ (if } \Delta q_i > 0)$$

$$= q_i^- \text{ (if } \Delta q_i < 0)$$

$$(1)$$

It is necessary to note that q_i^+ is taken equal to zero if $\Delta q_i < 0$ and similarly q_i^- is taken equal to zero if $\Delta q_i > 0$. The CT electronic excitation will thus result in two main categories of atoms. The atoms which lose electronic charge would have positive charge (q_i^+) upon excitation and the atoms which gain electronic charge and would have negative charge (q_i^-) upon excitation. The amount of charge transferred intra-molecularly can be calculated as

$$q^{CT} = \sum_i q_i^+ = |\sum_i q_i^-| \tag{2}$$

Two barycenters corresponding to the q_i^+ and q_i^- functions have been defined [12,13] by the Cartesian coordinates of the starting and ending points of the charge transfer process as:

$$r^{+} = (x^{+}, y^{+}, z^{+}) = \frac{\sum_{i} r_{i} q_{i}^{+}}{q^{CT}}$$
(3)

$$F^{-} = (x^{-}, y^{-}, z^{-}) = \frac{\sum_{l} r_{l} q_{l}^{-}}{q^{CT}}$$
(4)

Accordingly, the charge transfer distance is calculated as:

$$d^{CT} = |r^+ - r^-|$$
 (5)

The change in dipole moment of the molecule as a result of the electronic excitation is: $\Delta\mu^{CT} = d^{CT}q^{CT}$ (6)

1

For a rod-like system in which the CT predominantly takes place along the x-axis, an index denoted as H is defined as:

$$H = \frac{|\sigma^{+x} + \sigma^{-x}|}{2} \tag{7}$$

Where $\sigma^{\pm x}$ is the root mean square deviation for the positive or negative components along the x- axis calculated as:

$$\sigma^{\pm x} = \sqrt{\frac{\sum_i q_i^{\pm} (x_i - x^{\pm})^2}{q^{CT}}} \tag{8}$$

Two centroids of charges $C_+(r)$ and $C_-(r)$ associated to the positive and negative density regions respectively were defined for visualization purposes and a descriptor giving the difference between the calculated d^{CT} and H denoted as the t-index is defined [12,13] as:

$$t = d^{CT} - H \tag{9}$$

A code developed [13,51] to calculate these density model descriptors has been used in our calculations. Other criteria determining the efficiency of the DSSC such as light harvesting efficiency (LHE) of the sensitizing dyes were also calculated as described before [50]. All DFT and TD-DFT calculations were performed using G03 package [52]. Optimum molecular geometry and the electronic vertical excitation energies were calculated within the framework of TD-DFT approach.

The PBE functional [53] was utilized and the solvent effects were taken into account using the polarizable continuum model C-PCM [54-56]. The G03 generated cube files at this level of theory for the ground as well as excited states were utilized as input data into the code developed [13,51] to calculate the different CT transition descriptors defined above in this section.

RESULTS AND DISCUSSION

111

The calculated values of some selected geometrical parameters for all the studied dyes are collected in Table 1. The calculated average value of the metal-ligand nitrogen atom bond distance was found to be 1.88 for all the complexes

I Co(III),II Co(III),III Co(III) and IV Co(III). For the complexes I Ni(II),II Ni(II),

III Ni(II) and IV Ni(II) the average calculated value of this bond distance was found to be 1.90 while 1.96 for all the Cu(I) complexes and 2.03 for all the Zn(II) complexes with spacers I, II, III and IV respectively. This increase in the calculated value of this metal-nitrogen bond distance is consistent with the increase in van der Waals radii of the metal ions.

The calculated values of the bond angles N2-M-N14 , N29-M-N35 , N2-M-N35 and N14-M-N29 for all the studied complexes indicated that the geometry around the central metal ion are more or less distorted tetrahedral symmetry. It was found that the p-bromo benzene ring in all the studied complexes is twisted out of the plane of the neighboring pyridine ring (θ 1 and θ_2 shown in Fig 1) by a value averaged over all the studied metal complexes equal to 29.5°. It is worth noting that the dihedral angles D₁ and D₂ reported in table 1 give the twist angle between the planes of the two bi-pyridine ligands coordinated to the metal ion. The average calculated value of D1 was found to be 71.9° and that of D2 was found to be 86.2°. This indicates that the two planes of the two bi-pyridine ligands in all of the studied metal complexes are nearly perpendicular.

I II III IV I III IV I II	III IV							
Bond Distances (Å)								
1.87 1.89 1.87 1.87 1.89 1.89 1.89 1.90 1.95 1.95 1.95 2.04 2.02	2.02 2.03							
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 4							
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 6							
1.89 1.88 1.88 1.87 1.89 1.89 1.89 1.89 1.95 1.95 1.95 1.95 2.03 2.02	2.02 2.02							
M-N29 5 1 5 6 2 8 8 8 9 8 8 8 5 2	7 6							
1.88 1.87 1.87 1.88 1.90 1.89 1.89 1.89 1.96 1.95 1.95 1.95 2.03 2.02 2.04	2.02 2.02							
M-N35 1 4 7 4 2 8 9 6 0 8 9 9 0 2	8 5							
1.46 1.46 1.46 1.46 1.46 1.46 1.46 1.46 1.47 1.47 1.47 1.47 1.48 1.48 1.48	.48 1.48							
C28-C34 6 4 5 6 3 4 3 4 4 6 5 6 8 8	7 8							
Bond Angles (°)								
8								
5. 85.3 85.6 85.5 85.3 85.4 85.4 83.9 83.9 83.9 84.0 83.4 83.8	33.9 83.4							
N2-M-N14 6								
8	2.5 02.4							
5. 85.5 85.4 85.3 85.4 85.3 85.4 85.3 85.4 85.9 83.9 84.0 83.9 83.8 83.7 8	33.5 83.4							
N29-IN-IN35 5								
	18 118							
7.3 7.4 2.7 6.8 6.4 4.4 4.4	5 0							
N2-M-N35 8	0							
1								
0 109. 110. 110. 106. 106. 106. 106. 123. 123. 123. 123. 120. 118.	18. 117.							
9. 3 1 5 4 8 8 4 5 6 6 6 0 4	6 5							
N14-M-N29 2								
1 112. 113. 113. 113. 113. 113. 113. 114. 114	16. 116.							
	2 3							
N2-CI-CI3 5								
	16 116							
	2 0							
N29-C28-C34 6	- •							
Dihedral Angles (°)								
01 24.6 26.7 25.5 26.6 28.3 28.4 28.2 30.5 31.7 31.2 31.7 31.7 31.0 30.6	30.4 31.0							

Table 1 . Selected optimized geometrical parameters of the studied metal complex Dyes.

112

θ2	27.7	26.4	26.7	25.5	30.6	30.4	30.5	27.9	31.8	31.6	31.8	31.8	30.7	30.9	31.2	30.0
θ3	30.1	1.9	1.9	1.1	32.5	2.3	1.4	3.4	31.8	10.2	0.0	2.8	32.5	2.7	0.5	0.3
θ4	30.3	4.3	0.7	1.0	30.7	2.4	1.5	4.1	31.9	9.8	0.0	2.5	32.0	2.8	0.5	0.2
D1	79.5	78.9	78.4	78.7	70.4	70.1	70.2	69.8	90.1	90.4	90.1	90.3	96.6	79.9	99.0	77.8
D4	100.	101.	101.	101.	109.	109.	109.	110.	89.9	89.6	89.9	89.7	82.4	100.	81.0	102.
D2	5	1	6	3	6	9	8	2						1		2

For a better understanding of the nature of the charge transfer electronic transition in the studied metal complexes as sensitizing dyes in DSSCs the CT descriptors defined in the previous section have been calculated and reported in Table 2. The amount of charge transferred on going from the ground to the excited state q^{CT} was found to depend on the type of the metal as well as the π -linker used.

Table 2 . Calculated Descriptors for the charge transfer transitions of the studied metal complex dyes.

Dye	q _{CT} (e)	Dct(Ă)	μ _{CT} (Debye)	H(A°)	t(A°)
I (Co(III))	0.443	3.360	7.145	3.565	-0.205
II (Co(III))	0.370	2.572	4.571	3.420	-0.848
III (Co(III))	0.442	3.934	8.351	3.649	0.285
IV (Co(III))	0.459	3.871	8.523	3.527	0.344
I (Cu(I))	0.773	3.826	14.193	3.560	0.266
II (Cu(I))	0.587	2.643	7.451	3.007	-0.364
III (Cu(I))	0.839	3.530	14.208	3.242	0.289
IV (Cu(I))	0.924	3.469	15.387	3.488	-0.019
I (Ni(II))	0.718	2.307	7.955	3.190	-0.883
II (Ni(II))	0.718	1.043	3.595	3.037	-1.994
III (Ni(II))	0.691	1.423	4.718	3.1405	-1.717
IV (Ni(II))	0.642	1.493	4.601	3.272	-1.779
I (Zn(II))	1.323	7.301	46.368	4.294	3.007
II (Zn(II))	1.341	5.931	38.178	3.851	2.081
III (Zn(II))	1.304	7.449	46.626	4.166	3.284
IV (Zn(II))	1.301	7.744	48.343	4.315	3.429

For the Co(III) complexes with the ligands I, II, III and IV the calculated q^{CT} ranges from 0.38-0.46 (e). This range is found to be higher for the Ni(II) complexes being 0.64-0.72 (e). The calculated values of q^{CT} for the Cu(I) complexes and the Zn(II) complexes lie in the ranges 0.59-0.92 (e) and 1.30-1.34 (e) respectively. The largest calculated value of q^{CT} among the four complexes of each metal ion benzene, pyrrole, furan and thiophene π -linkers was found to increase in the order Co(III) < Ni(II) < Cu(I) < Zn(II) complexes. For Co(III) and Cu(I) complexes the thiophene π -linker between the metal and 2-cyanoacrylic acid acceptor group, was found to be the best in enhancing the CT process where the calculated q^{CT} values were found to be ~ 0.46 e and ~ 0.92 e for these complexes respectively (Table 2). On the other hand the largest calculated value of q^{CT} for Ni(II) and Zn(II) complexes was found with the pyrrole moiety as the π -linker between the metal and 2-cyanoacrylic acid acceptor group. Its calculated values were found to be ~ 0.72 (e) and 1.34 (e) respectively. As mentioned above the calculated values of q^{CT} for Zn(II) complexes range 1.30 -1.34 (e) for the four π -spacers used. The difference is only 0.04 (e) which is not a determining factor. However, this is an unexpected overestimation of the amount of charge transferred upon electronic excitation (the q^{CT} descriptor). This unphysical large q^{CT} calculated value (~ 1.30 e) could be related to the accuracy of the sampling of the density over a grid [12].

The calculated CT length which is the distance between barycenters (d^{CT}) did not show a systematic trend with respect to the type of the π -spacer assigned. The order of increase or decrease depends only on the type of metal ion and not the π -spacer group. The largest calculated CT length for Co(III) complex was calculated to be ~3.90 Å with thiophene as well as furan as the π -spacer. For Ni(II) complexes the largest calculated CT length was found to be 2.30 Å with benzene moiety as the π -spacer. For Cu(I) complexes the calculated largest distance was found to be 3.83 Å with also the benzene moeity as the π -spacer. For the complexes of Zn(II) the two centroids were found to be much more extended over the molecule so that the largest calculated CT distance was found to be amounting to 7.74 Å with thiophene as the π -spacer.

On the other hand the calculated change in molecular dipole moment upon going from the ground to the excited state μ^{CT} (Table 2) showed a more or less systematic trend. The highest calculated value of μ^{CT} for all the metal complexes was found with the thiophene moiety as the π -spacer except for Ni(II) complexes where the benzene π -linker have given the highest calculated μ^{CT} value. The calculated μ^{CT} values showed the trend thiophene > furan >

benzene > pyrrole for the Co(III), Cu(I) and Zn(II). For Ni(II) complexes the trend was found to be more or less the same, being benzene > furan > thiophene > pyrrole where benzene and thiophene have exchanged position. It is worth noting that different atomic charge models were tested [13] and it is found that the difference of dipole moments between the ground and excited states was reproduced by most approaches used [13], however no atomic charge model was fully satisfactory for reproducing the distance. Furthermore it has been concluded [13] that for the more complex DSSC dyes the different partial atomic charge models used were able to provide CT parameters that were systematically on the density reference spot. The above discussed variations of calculated q^{CT} and d^{CT} for the different metal complexes as the π -spacer is changed from benzene to pyrrole, furan and thiophene moieties are shown in (Fig 2) and the computed centroids which show the spatial extent of the overlap between the density depletion and the increment regions are also shown in Fig 3, where the extents of spatial proximity between the donor and acceptor parts of the different dyes investigated are shown.



Fig 2. (a) Calculated amount of Charge transferred (qCT) (b) Calculated Charge transfer distance (D_{CT})



 $\begin{array}{ll} \mbox{Fig. 3. PBE/6-31G} & \mbox{Computed differences in total density for the ground and excited states } [\Delta \ \rho \ (r)], \mbox{graphical} & \mbox{representation of} \\ & \mbox{D}_{CT}, \mbox{ and centroids of charge } (C+/C) \ for all the studied metal complex dyes in THF as solvent. \end{array}$

Comparison between the calculated d^{CT} and H values for the studied metal complex dyes showed that for nearly all the π -spacers investigated and in most of the Co(III) and Ni(II) metal complex dyes the calculated d^{CT} values were found to be smaller than the calculated H values. On the other hand for Cu(I) and Zn(II) metal complex dyes the calculated d^{CT} values are larger than the calculated H values. These findings points out the presence of a through-space charge transfer in these dyes. The index t (eqn. 9) could also be used to feature the extent of through-space character of a given electronic transition. It has been pointed out [12] that a value t > 1.6 Å indicates that a potentially problematic transition for standard GGA and hybrid functionals.

The absorption band wavelength (λ_{max}), oscillator strength (f) and main electronic excitations contributing for the first three absorption bands for all the studied metal complex dyes were calculated by the TD-DFT method and the results are reported in Tables (3,4). All the studied dyes have an intense band corresponding to the intramolecular

CT absorption band. The electronic excitation which was found to have the main contribution to the most intense absorption band for all the systems studied was found to originate from the (HOMO), (HOMO-1) or the (HOMO-2) levels to the LUMO level.

metal	spacer	$\lambda_{max}(nm)$	Main Excitation	f	LHE
		2875.3	HOMO to LUMO (0.7072)	0.0514	0.1116
	Ι	2750.5	HOMO-2 to LUMO (0.7068)	0.0006	0.0014
		1944.1	HOMO-1 to LUMO(0.6632)	0.1330	0.2638
		2581.9	HOMO to LUMO(0.6866)	0.0455	0.0995
	II	2157.3	HOMO-1 to LUMO(0.5685)	0.0477	0.1040
C-(III)		1856.5	HOMO-3 to LUMO(0.6107)	0.2011	0.3706
C0(III)		2736.6	HOMO to LUMO(0.7121)	0.0539	0.1167
	III	2011.0	HOMO-1 to LUMO(0.6099)	0.0988	0.2035
		1838.7	HOMO-2 to LUMO(0.6614)	0.0982	0.2024
	IV	2713.5	HOMO to LUMO(0.7107)	0.0530	0.1149
		1969.9	HOMO-1 to LUMO(0.4951)	0.0741	0.1569
		1854.5	HOMO-2 to LUMO(0.5426)	0.1524	0.2960
		816.0	HOMO to LUMO (0.6741)	0.0000	0.0000
	Ι	711.3	HOMO-1 to LUMO+1 (0.6734)	0.0000	0.0000
		660.7	HOMO-1 to LUMO (0.5826)	0.5829	0.7387
		803.8	HOMO-1 to LUMO (0.6203)	0.0000	0.0000
	II	730.3	HOMO to LUMO+1 (0.6196)	0.0000	0.0000
C ₂ (I)		658.7	HOMO to LUMO (0.5771)	0.6146	0.7571
Cu(I)	ш	883.0	HOMO to LUMO (0.6954)	0.0000	0.0000
		771.9	HOMO to LUMO+1 (0.7061)	0.0000	0.0000
		686.1	HOMO-1 to LUMO (0.6148)	0.4825	0.6708
		943.3	HOMO to LUMO (0.7001)	0.0000	0.0000
	IV	852.8	HOMO to LUMO+1 (0.7063)	0.0000	0.0000
		725.8	HOMO-1 to LUMO (0.6300)	0.4261	0.6251

 $Table \ 3. \ Calculated \ (\lambda_{max}), oscillator \ strength \ (f) \ , main \ excitation \ and \ light \ harvesting \ efficiency \ for \ Co(III) \ and \ Cu(I) \ dyes \ calculated \ dyes \ dys \ dys \ dyes \ dyes$ by TD-DFTmethod.

Table 4. Calculated (λ_{max}) , oscillator strength (f), main excitation and light harvesting efficiency for Ni(II) and Zn(II) dyes calculated by TD-DFTmethod.

metal	spacer	λ_{max} (nm)	Main Excitation	f	LHE
		1041.4	HOMO to LUMO (0.6787)	0.0373	0.0823
	I	974.1	HOMO-1 to LUMO (0.5535)	0.0188	0.0424
		872.6	HOMO-2 to LUMO (0.6076)	0.0062	0.0142
		1140.3	HOMO to LUMO (0.6923)	0.0486	0.1059
	II	1059.0	HOMO-1 to LUMO (0.6162)	0.0292	0.0650
NP(II)		932.0	HOMO-2 to LUMO (0.5868)	0.0151	0.0342
INI(11)		1078.1	HOMO to LUMO (0.6884)	0.0452	0.0988
	III	981.0	HOMO-1 to LUMO (0.5588)	0.0216	0.0485
		923.0	HOMO-2 to LUMO (0.5731)	0.0140	0.0317
	IV	1073.5	HOMO to LUMO (0.6883)	0.0503	0.1094
		979.1	HOMO-1 to LUMO (0.5624)	0.0222	0.0498
		921.4	HOMO-2 to LUMO (0.5779)	0.0145	0.0328
	Ι	513.5	HOMO to LUMO (0.7066)	0.0003	0.0007
		508.1	HOMO-1 to LUMO (0.7065)	0.0005	0.0012
		461.2	HOMO-1 to LUMO+1 (0.6916)	0.2013	0.3709
	п	533.2	HOMO to LUMO+1 (0.6880)	0.0008	0.0018
		519.9	HOMO-1 to LUMO+1 (0.6889)	0.0008	0.0018
7 n(II)		498.0	HOMO to LUMO (0.6469)	0.2054	0.3768
Zn(11)	ш	546.2	HOMO to LUMO (0.7070)	0.0003	0.0007
		540.3	HOMO-1 to LUMO (0.7070)	0.0004	0.0009
		464.1	HOMO-1 to LUMO+1 (0.5883)	0.2990	0.4977
		562.5	HOMO to LUMO (0.7071)	0.0002	0.0005
	IV	556.2	HOMO-1 to LUMO (0.7071)	0.0002	0.0005
		480.5	HOMO-2 to LUMO (0.5934)	0.1413	0.2777

The light harvesting efficiency (LHE) for all the studied dyes have been calculated using the following equation [57, 58]:

$$LHE = 1 - 10^f \tag{10}$$

especially for the calculated most intense absorption band. The calculated LHE values are summarized in Tables (3,4). The results showed that the Cu(I) complexes with the pyrrole moiety as the π -spacer has the highest calculated LHE value, being ~ 0.76. The lowest LHE calculated value was found to be 0.08 for the Ni(II) complex with benzene as the π -linker. The Zn(II) complex with furan π -linker has a calculated LHE value of 0.5 while 0.37 for the Co(III) complex with pyrrole as the π -spacer group. Thus the order of calculated LHE values is increasing as Cu(pyrrole) > Zn(furan) > Co(pyrrole) > Ni(thiophene). For the Cu(I) and Co(III) complex dyes the calculated LHE values are corresponding to the electronic excitations (HOMO-1) \rightarrow LUMO while HOMO \rightarrow LUMO for the Ni(II) complexes, and finally to the (HOMO-1) \rightarrow (LUMO+1) excitation for the Zn(II) complex dyes.

CONCLUSION

1- The amount of charge transferred on going from the ground state to the excited state (q^{cT}) was found to depend on the type of the π -linker used as well as themetal. For all the spacers used q^{cT} increased in the order Co(III) < Ni(II) <Cu(I) < Zn(II) metal complex dyes. For Co(III) and Cu(I) complexes the thiophene π -linker between the metal and the 2-cyanoacrylic acid acceptor group, was found to be the best in enhancing the CT process where the calculated q^{CT} values were found to be ~ 0.46 e and ~ 0.92 e for these complexes respectively. On the other hand the largest calculated value of q^{CT} for Ni(II) andZn(II) complexes was found with the pyrrole moiety as the π -linker between themetal and 2-cyanoacrylic acid acceptor group. The calculated values of q^{CT} forZn(II) complexes range from 1.30 -1.34 (e) for the four π -spacers used. Thisunexpected overestimation of the amount of charge transferred upon electronic could be related to the accuracy of the sampling of the density over a grid [12].

2- No systematic trends are found in the calculated values of d^{CT} with respect to thetype of the π -spacer assigned , however the calculated μ^{CT} values showed thetrend thiophene > furan > benzene > pyrrole for the Co(III) , Cu(I) and Zn(II) complexes . The trend was found to be more or less the same for Ni(II) metal complexes, being benzene > furan > thiophene > pyrrole . This could be related to the previous finding [13] that no atomic charge model was fully satisfactory for reproducing the distance .

3- The order of calculated LHE values is increasing as Cu(pyrrole) > Zn(furan) > Co(pyrrole) > Ni(thiophene). For Cu(I) and Co(III) complex dyes the calculated LHE values are corresponding to the electronic excitations (HOMO-1) \rightarrow LUMO while HOMO \rightarrow LUMO for the Ni(II) complexes and Finally to the (HOMO-1) \rightarrow (LUMO+1) excitation for the Zn(II) complex dyes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere.

CONTRIBUTION OF THE AUTHORS

Basant A. Ali with the help of Yasser R. Elmarassi performed the computations. Yasser R. Elmarassi monitored data collection and tabulation. Basant A. Ali monitored data collection and tabulation. Yasser R. Elmarassi analysed the data. Ahmed A. Hasanein analysed the data and drafted and revised the paper. Ahmed A. Hasanein and Yasser R. Elmarassi initiated the collaborative project, designed data collection, drafted and revised the paper and approved the final version.

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