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Research Article

## Charge Transfer Complexes of Recently Synthesized Mixed AzaThia Crown Ether and Pyridine Based Mixed AzaThia Crown Ether with Iodine and DDQ in Chloroform Solution

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**Abstract:** The interaction of two recently synthesized mixed azathia crown ether 1,7-dithia–10-aza-12-crown-4, and pyridine based mixed azathia crown ether with iodine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) have been examined in chloroform. Thermodynamics of these reactions are studied spectrophotometrically, and the formation of both 1:1 and 2:1 ( $[L]/[I_2]$ ) and  $[L]/[DDQ]$  complexes with iodine and DDQ was established. The complex formation constants  $K_f$  were determined by computer fitting of the absorbance-mol ratios data. Formation of the CT complexes of macrocycles with iodine and DDQ was confirmed by NMR and IR spectroscopies.

**Key words:** 1,7-dithia–10-aza-12-crown-4, Iodine, DDQ, thermodynamic, charge transfer.

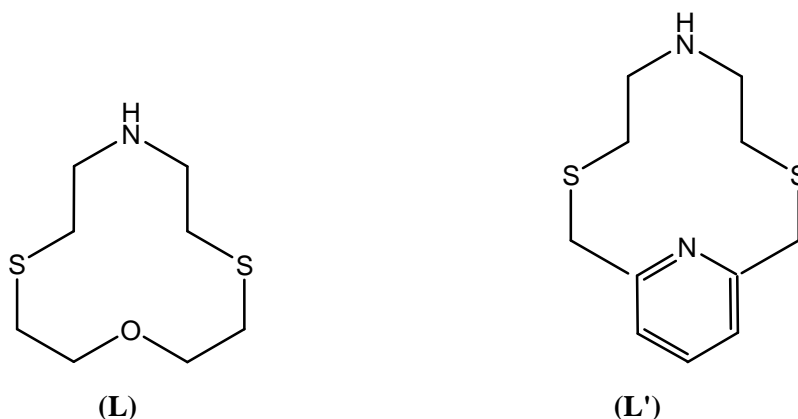
### INTRODUCTION

Electron donor-acceptor (EDA) or charge transfer complexes (CT) are recently gaining importance as potential high efficiency nonlinear optical materials<sup>1-3</sup>, organic super conductors<sup>4</sup> as well as photocatalysts<sup>5</sup>. EDA interaction is also important in the field of drug-receptor binding mechanism<sup>6</sup>, in solar energy storage<sup>7</sup> and surface chemistry<sup>8</sup> as well as many biological fields<sup>9</sup>.

Among the most interesting developments in chemistry has been the synthesis of macrocyclic polyethers<sup>10</sup>. These comprise a large group of cyclic compounds which can bind metal ions by entrapment

within an electron-rich cavity created by its inward-oriented donor atoms. The intense interest in the macrocyclic ligands centers on the extraordinary stability of their cation complexes and their peculiar ability to selectively bind certain cations in preference to others. Generally, nitrogen-containing heterocyclic compounds are of especial interest as electron donors. Iodine has been found to form with a variety of donor charge-transfer complexes whose properties have been thoroughly studied<sup>11</sup>. In the past decade, increasing attention has been paid to the molecular complexes of iodine with macrocyclic crown ethers and their aza derivatives in various solvents the result of these studies have clearly revealed that the substitution of the donating oxygen atoms in a crown ether ring by NH groups results in a drastic increase in the stability of the iodine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) complexes<sup>12-17</sup> over those of ordinary crowns<sup>18</sup>.

In this work we report the results of spectral studies of interactions of iodine and DDQ with recently synthesized mixed azathia crown ethers: macrocycle (L) and macrocycle (L').



## EXPERIMENTAL

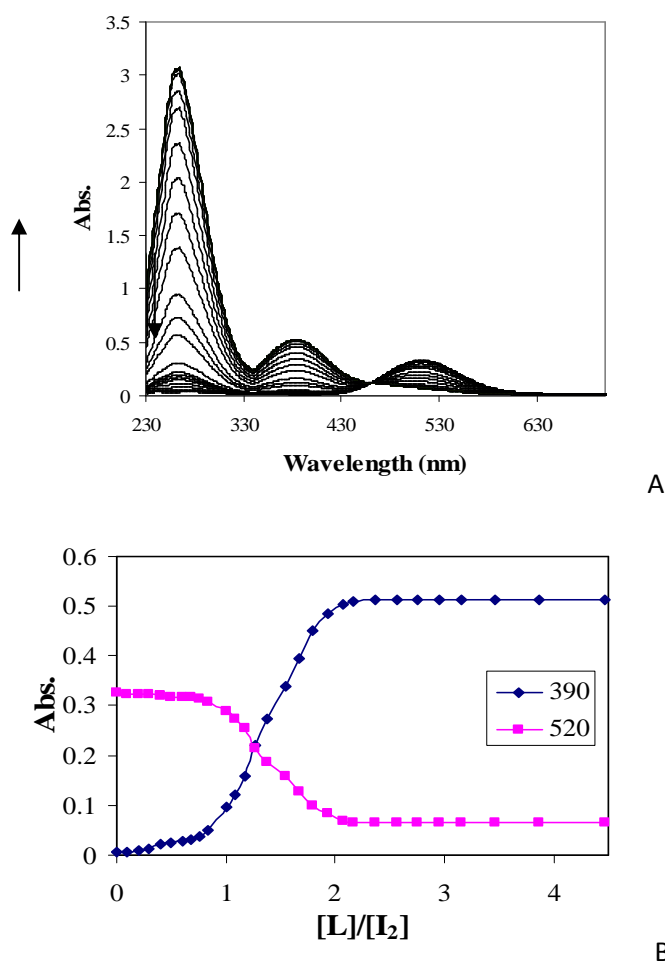
Reagent grade iodine (Merck) and DDQ (Aldrich) were of the highest purity available and the macrocycles (L) and (L') were synthesized by V. Lippolis and co-workers at university of Cagliari used without any purification, except for vacuum drying. Reagent grade chloroform (Aldrich) was used as received. All UV-Vis. Spectra were recorded on a computerized CECIL 9000 instrument equipped with a HUBER polystate temperature controller, using a 10-mm quartz cell, at the desired temperature  $\pm 0.1$  °C.

The proton NMR spectra were recorded on an AVANCE Spectrometer with field strength of 4.7 T. In all experiments, TMS was used as an internal standard. The IR spectra were recorded on a Shimadzo – IR-470 spectrometer.

## RESULTS AND DISCUSSION

**Iodine complexes:** Two series of solutions, the first containing  $3.6 \times 10^{-4}$  M iodine in chloroform in the presence of an increasing amounts of macrocycle (L) and the second containing  $3.1 \times 10^{-4}$  M iodine in chloroform in the presence of an increasing amounts of macrocycle (L') were prepared and allowed to reach equilibrium. Then, the electronic absorption spectra of the solutions were recorded at 10.0, 17.0, 25.0 and 32.0 ( $\pm 0.1$ )°C. Sample absorption spectra for the macrocycle (L) at 25°C are shown in Fig.1.A. As it is obvious from this Figure, while macrocycle shows no measurable absorption in the (240 – 640) nm spectral region, iodine has an absorption band in 510 nm. Addition of macrocycle (L) to the iodine solution results in two strong absorption bands located in the 230-430 nm regions. The first absorption, located at about 266 nm, corresponds to a charge transfer band and the second at 380 nm is

the blue shifted iodine band<sup>19</sup>. Thus the appearance of these new bands upon mixing of the two reactants in chloroform must be associated with the formation of a donor – acceptor complex in solution<sup>20, 21</sup>. The stoichiometry of the charge-transfer complex, as determined by the mole ratio method<sup>22</sup>, was found to be  $L_2A_2$  and  $L_2A$ . (The L and A refers to donor ligand (macrocycle), and acceptor (iodine) respectively) Moreover, the existence of a well-defined isosbestic point at 462 nm in the spectra of iodine upon titration with macrocycle is also in support with simple complexation equilibrium in solutions. As it is obvious from Figure 1.A while the intensity of the 380 nm band increases with increasing  $[\text{macrocycle(L)}]/[\text{I}_2]$  mole ratio it results in decreasing intensity of 510 nm band, of iodine. The plot of absorbance vs.  $[\text{macrocycle(L)}]/[\text{I}_2]$  mole ratio at 390 nm and 520 nm are shown in Fig.1.B. It is quite obvious that macrocycle forms two kinds of complexes with Iodine  $L_2I^+-I_3^-$  and  $L_2I^+-I^-$ .

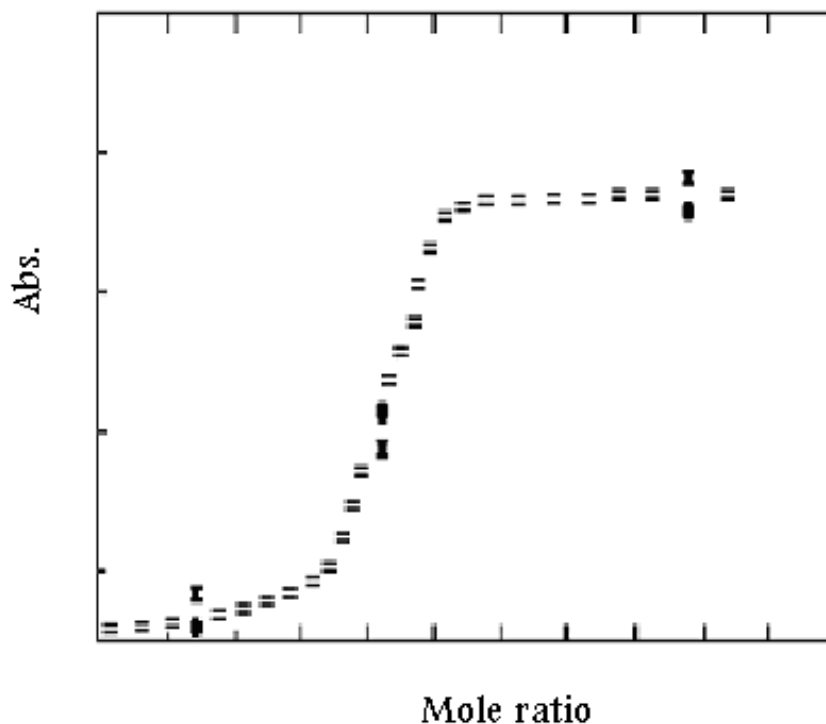


**Fig. 1 :** (A) Electronic absorption spectra of  $3.6 \times 10^{-4}$  M of iodine in the presence of increasing amounts of macrocycle (L) in chloroform solution at 25.0 °C. The  $[\text{L}]/[\text{I}_2]$  mole ratios are: (1) 0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4, (6) 0.5, (7) 0.6, (8) 0.68, (9) 0.76, (10) 0.83, (11) 1.0, (12) 1.08, (13) 1.17, (14) 1.27, (15) 1.38, (16) 1.54, (17) 1.67, (18) 1.80, (19) 1.94, (20) 2.07, (21) 2.16, (22) 2.36, (23) 2.56, (24) 2.76, (25) 2.96, (26) 3.16, (27) 3.46, (28) 3.87, (29) 4.47. (B) corresponding absorbance vs.  $[\text{L}]/[\text{I}_2]$  plot, ( $\lambda = 390$  and 520 nm).

The appearance of chemical shift from 0.1 to 0.6 ppm in C-H bonds adjacent to S and N hetero atoms in NMR spectra and from 10 to 120  $\text{cm}^{-1}$  shift in frequencies of  $-\text{N}-\text{CH}_2$ ,  $-\text{S}-\text{CH}_2$  and  $-\text{O}-\text{CH}_2$  bonds

reveals the formation of new complex in solution. The  $^1\text{H}$  NMR spectra and IR spectra are not shown here. All details directed in Tables 4 and 6.

The existence of a well-defined isosbestic point at about 462 nm in Fig.1 and data from IR and NMR spectra (Table 4 and 6) established the formation of these complexes obviously. Practically, the formation of the resulting charge-transfer adduct can easily be noticed in solution by the observation of two new strong absorption bands in the UV-Vis spectra of the donor-acceptor mixtures, which can be used to evaluate the formation constant of the  $2\text{D} + \text{I}_2 = \text{D}_2\text{I}^+ - \text{I}^-$  and  $2\text{D} + 2\text{I}_2 = \text{D}_2\text{I}^+ - \text{I}_3^-$  equilibrium.



**Fig. 2:** Computer-fitted curve for charge transfer complexation of macrocycle (L) with iodine (Fig.1.B). Points (o), (x) and (=) indicate theoretical, experimental and good agreement between theoretical and experimental points, respectively

**Evaluation of  $K_f$  values:** When a ligand, as a donor (L), reacts with an acceptor (A), it may form either a 1:1 complex, LA (model **I**), or both 1:1 and 1:2 complexes,  $\text{L}_2\text{A}$ , (model **II**). The mass balance equations of the two possible models in solution, shown in Table 1, can be solved to obtain equations for the free ligand concentration, [L], or acceptor concentration [A] (Table1).

The observed absorbance of solution is also given by:

$$A_{\text{obs}} = \varepsilon_{\text{LA}} [\text{LA}] \quad (\text{I})$$

$$A_{\text{obs}} = \varepsilon_{\text{LA}} [\text{LA}] + \varepsilon_{\text{L}_2\text{A}} [\text{L}_2\text{A}] \quad (\text{II})$$

**Table- 1:** Mass-balance equations and solutions used in the computer program for evaluation of photometric data

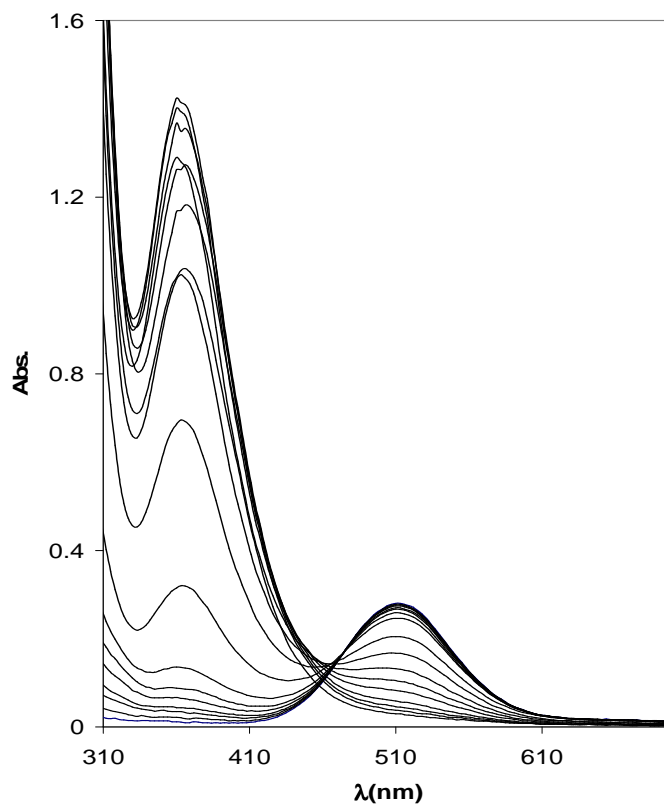
Reactions	Stability constants	Mass-balance equns.	Solution
(I) $A+L=LA$	$K_1=[LA]/[L][A]$	$C_A=[A]+[LA]$ & $C_L=[L]+[LA]$	$K_1[L]^2+(1+K_1(C_A-C_L))[L]-C_L=0$
(II) $A+L=LA$	$K_1=[LA]/[A][L]$	$C_A=[A]+[LA]+[AL_2]$	
(III) $LA+L=L_2A$	$K_2=[L_2A]/[LA][L]$	$C_L=[L]+[LA]+2[L_2A]$	$K_1K_2[L]^3+K_1(1+K_2(2C_A-C_L))[L]^2+(1+K_1(C_A-C_L))[L]-C_L=0$

Where  $\epsilon$  values are the molar absorptivities of the species denoted. At the wavelength utilized the free A and free ligand does not contribute significantly to the solution absorbance. Based on each case (type of ligand), one of the above mentioned mass balance equations will be used for evaluation of stability constant. In this case we used the model (II) for both iodine and DDQ complexes.

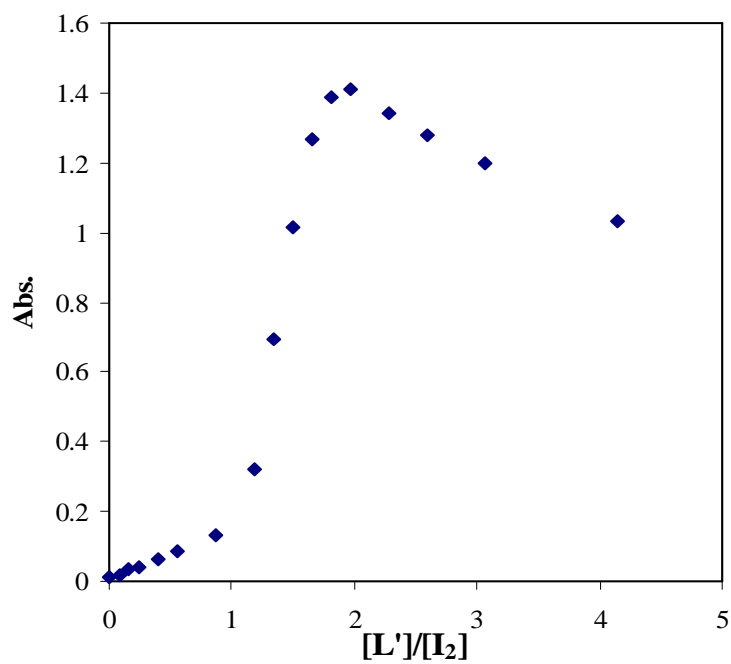
The formation constants of the resulting  $L_2A_2$  and  $L_2A$  complexes at various temperatures were determined by computer fitting of the absorbance measurements at 390 nm for a series of 29 solutions with varying concentration of macrocycle (L) and constant iodine ( $3.6 \times 10^{-4}$  M) in chloroform by means of previously described program, (KINFIT)<sup>23</sup>. A sample computer fitted curve for charge transfer complexation of macrocycle (L) with iodine was shown in Fig.2. All the formation constants evaluated for the macrocycle (L)-I<sub>2</sub> complexes at various temperatures are listed in Table 2. Details of NMR and IR spectrum are directed in Tables 4 and 5.

Sample absorption spectra of the second series of solutions (macrocycle (L')-I<sub>2</sub>) are shown in Fig.3. The macrocycle has an absorption band at 275 nm and has no measurable absorbance over 310 nm, and iodine band is at 510 nm. This figure clearly shows upon addition of ligand to iodine solution, the resulting complexes have two rather sharp absorptions, the first one located at 360 nm and the second below 310 nm (not included in the figure because this band is overlapped with the absorption of the macrocycle at high concentrations of macrocycle). As it is obvious from this figure, while the intensity of 520 nm band of iodine decreases with increasing [macrocycle(L')]/[I<sub>2</sub>] mole ratio it results in increased intensity of 390 nm band of new complex through an isobestic point at 466 nm until [macrocycle(L')]/[I<sub>2</sub>] mole ratio of 1.0 where beyond it the isobestic is deviated due to formation of the second type of complex, the inflection in mole ratio plot at the [macrocycle(L')]/[I<sub>2</sub>] = 1 and 2, clearly shows the formation of  $L_2A$  as well as LA in solution. The mole ratio plots at 366 nm and 516 nm are shown in Fig.4. As it is obvious from this figure the mole ratio plots at 516 and 366 nm support the formation of these two types of complexes in solution.

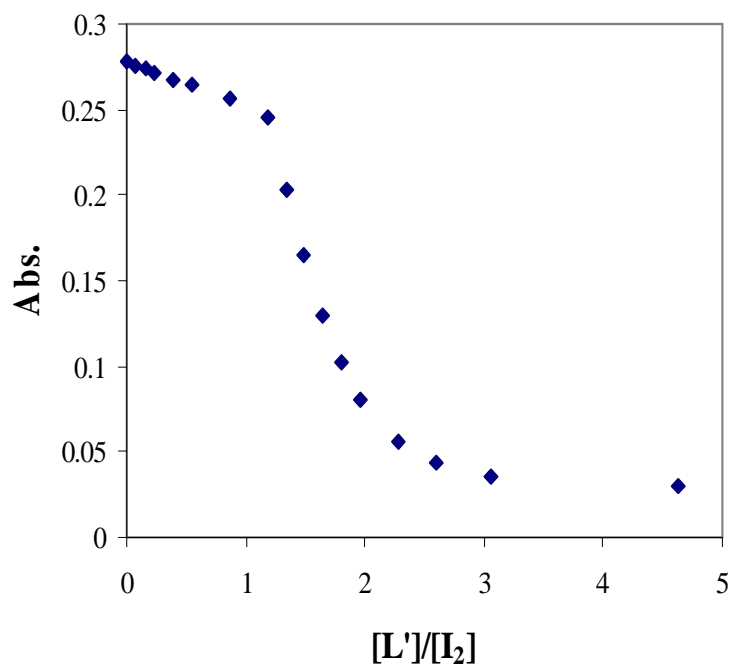
The formation constants of the resulting  $L_2A_2$  and  $L_2A$  complexes at various temperatures were determined by computer fitting of the absorbance measurements at 520 nm for a series of 17 solutions with varying concentration of macrocycle (L') and constant concentration of iodine ( $3.1 \times 10^{-4}$  M) in chloroform by means of previously described method (KINFIT)<sup>23</sup>. All the formation constants evaluated for the macrocycle (L')-I<sub>2</sub> complexes at various temperatures are listed in Table 3. Details of NMR and IR spectrum are directed in Tables 5. and 6.



**Fig. 3:** Electronic absorption spectra of  $3.1 \times 10^{-4}$  M iodine in the presence of increasing concentration of macrocycle ( $L'$ ) at  $24^\circ\text{C}$ . The  $[L']/[I_2]$  mole ratios are : 0, 0.08, 0.15, 0.23, 0.40, 0.55, 0.86, 1.18, 1.33, 1.49, 1.65, 1.80, 1.97, 2.27, 2.59, 3.06, 4.15.



A



B

**Fig. 4: Plots of absorbance vs. mole ratio of  $[L']/[I_2]$  in  $CHCl_3$  solution at  $24^\circ C$ . A) at  $366\text{nm}$  B) at  $516\text{ nm}$ .**

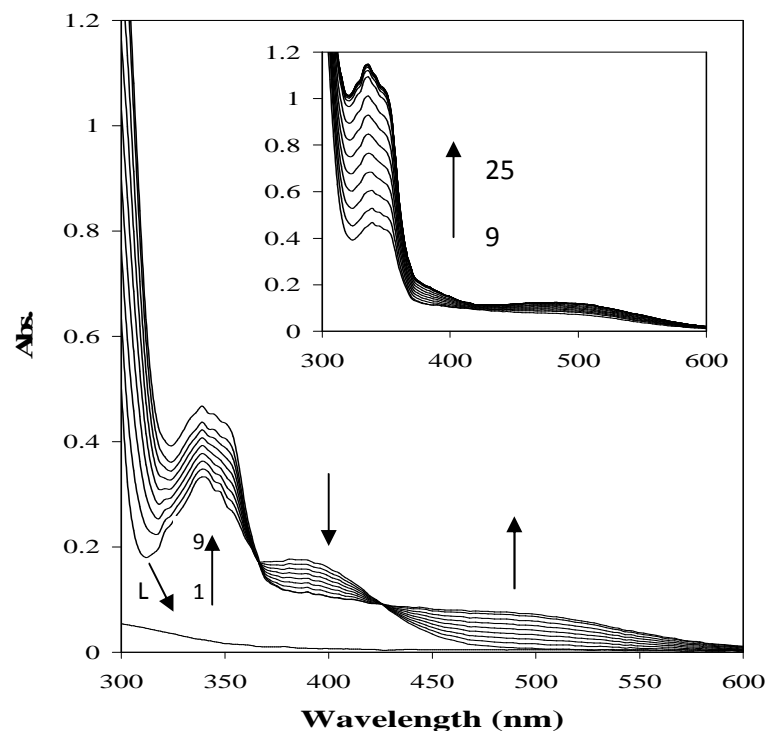
**DDQ Complexes:** In order to study the complex formation reaction of macrocycles with DDQ, two series of solutions the first containing  $2.4 \times 10^{-4}$  M DDQ in chloroform in the presence of an increasing amounts of macrocycle (L) and the second containing  $3.3 \times 10^{-4}$  M DDQ in the presence of an increasing amounts of macrocycle (L') were prepared and allowed to reach equilibrium. The electronic absorption spectra of the solutions were recorded at  $10.0$ ,  $17.0$ ,  $25.0$  and  $32.0 (\pm 0.1)^\circ C$ . Sample absorption spectra for macrocycle (L) at  $25^\circ C$  are shown in Fig.5. Increasing the absorption bands at about  $500$  and  $339$  nm and decreasing of absorption in  $400$  nm until  $[L]/[DDQ]$  mole ratio reaches  $1.0$ , and a large increase in absorption band in  $339$  nm for mole ratios of  $[L]/[DDQ]$  from  $1$  to  $2$  clearly shows that two kinds of complexes with different stoichiometry are formed. The stoichiometry of the charge-transfer complexes, as determined by the mole ratio method<sup>22</sup>, was found to be L- DDQ and  $L_2$ - DDQ.

The plot of absorbance vs. [macrocycle (L)]/[DDQ] mole ratios at  $339$  nm is shown in Fig.6.B, and in some other wavelengths in Fig.6.A. It is obvious that two kinds of complexes between macrocycle (I) and DDQ, L-DDQ and  $L_2$ -DDQ are formed.

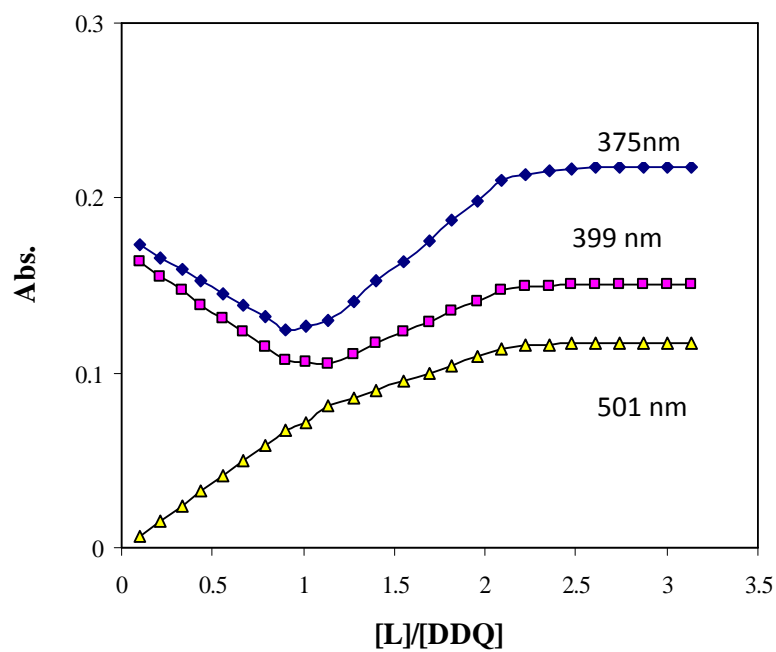
NMR studies of macrocycle (L) in the absence and presence of DDQ with different mole ratios revealed that hydrogen atoms attached to carbons adjacent to hetero atoms in L-DDQ and  $L_2$ -DDQ stoichiometries show chemical shift from  $0.1$  to  $0.23$  ppm.

The IR spectra showed  $20$  to  $120\text{ cm}^{-1}$  shift for C-H band frequencies of carbon atoms adjacent to hetero atoms (not included). Details directed in Table6.

The existence of two isobestic points at  $363$  nm and  $429$  nm (Fig. 5) until mole ratio of one and other data from IR and NMR spectrum prove the formation of these complexes L- DDQ and  $L_2$ - DDQ obviously (Tables 4 and 5).

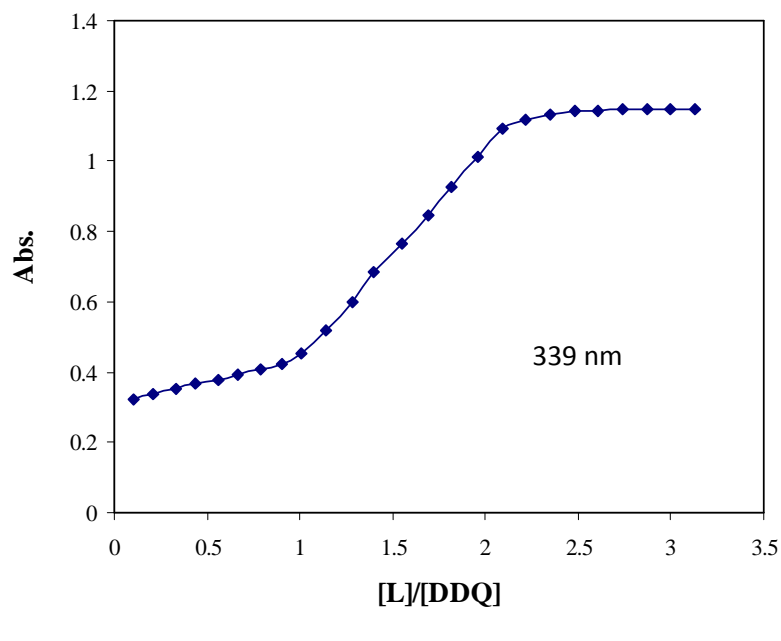


**Fig. 5:** Electronic absorption spectra of DDQ ( $2.4 \times 10^{-4}$  M) in the presence of increasing amounts of macrocycle (L) at  $\text{CHCl}_3$  at  $25^\circ\text{C}$ . The  $[\text{macrocycle (L)}]/[\text{DDQ}]$  mole ratios are: (1) 0.1, (2) 0.21, (3) 0.33, (4) 0.44, (5) 0.56, (6) 0.67, (7) 0.79, (8) 0.9, (9) 1.01, (10) 1.14, (11) 1.28, (12) 1.40, (13) 1.55, (14) 1.69, (15) 1.82, (16) 1.96, (17) 2.09, (18) 2.22, (19) 2.35, (20) 2.48, (21) 2.61, (22) 2.74, (23) 2.87, (24) 3.0, (25) 3.13.



A

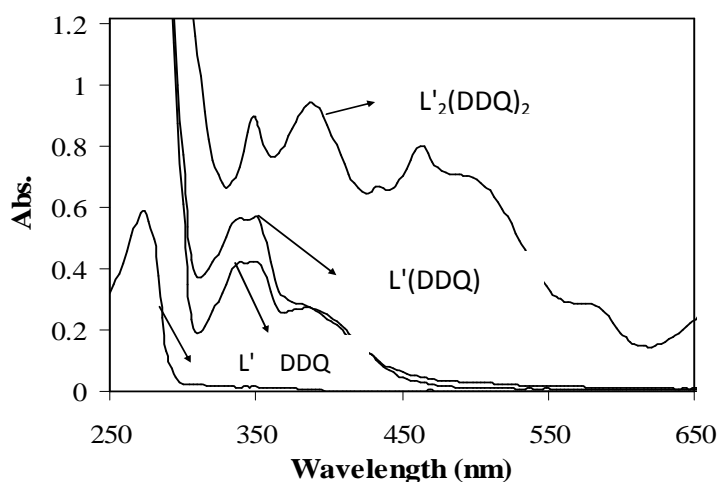




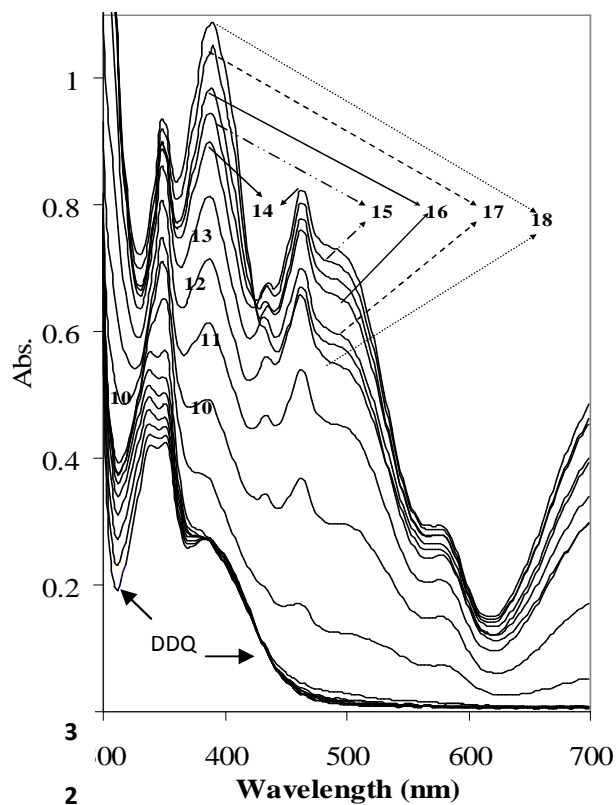
**Fig. 6: Mole ratio plots for titration of DDQ with macrocycle (L) in chloroform at 25°C (the  $\lambda$  values are A) 375, 399 and 501 nm and B) 339 nm.**

The formation constants  $K_f$  values are evaluated from the absorbance vs.  $[L]/[DDQ]$  mole ratio with previously described method. The results are directed in Table 2. The electronic absorption spectra for L' and its complexes with DDQ are shown in Fig. 7, clearly showing two different type of complexes.

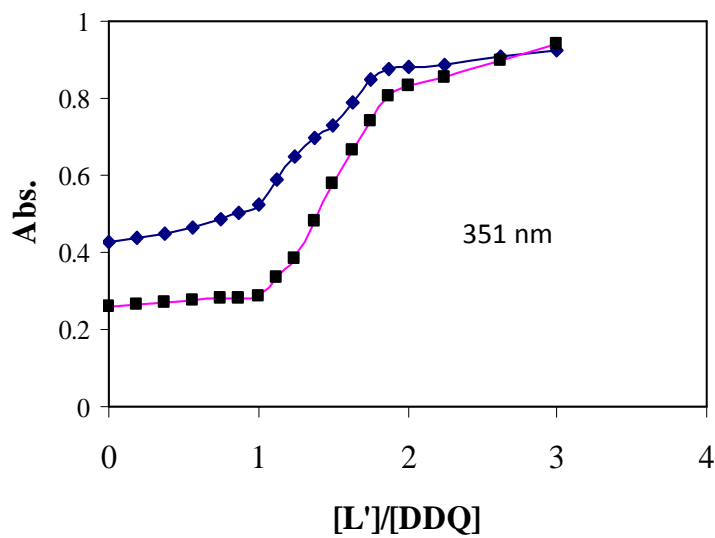
Absorption spectra for macrocycle (L') at 25°C are shown in Fig. 8, a new wide band consists of some sharp maximum absorptions in the region of 320-580 was observed. Thus the appearance of these new bands upon mixing of the two reactants in chloroform must be associated with the formation of a donor-acceptor complex in solution<sup>20-21</sup>. The stoichiometry of the charge-transfer complex, as determined by the mole ratio method<sup>22</sup>, was found to be L'-DDQ and L'<sub>2</sub>-DDQ. Moreover, the existence of a well-defined isobestic point at 429 nm in the spectra of DDQ upon titration with macrocycle is also in support of simple complexation equilibrium in solution (Fig. 8).



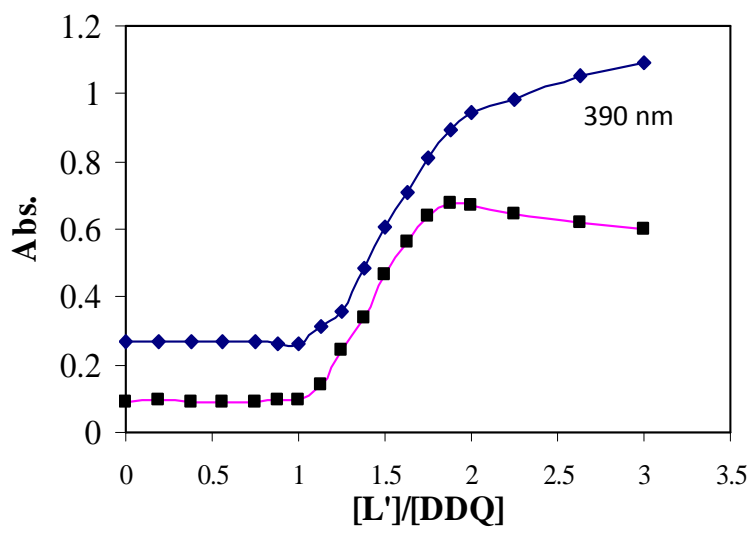
**Fig. 7: Electronic absorption spectra for macrocycle (L') and its complexes with DDQ in chloroform solution.**



**Fig. 8:** Electronic absorption spectra of  $3.3 \times 10^{-4}$  M DDQ in the presence of increasing concentration of macrocycle (L') at 33°C. The  $[\text{macrocycle(L')}] / [\text{DDQ}]$  mole ratios are: (1): 0, (2): 0.2, (3): 0.43, (4): 0.65, (5): 0.86, (6): 1.0, (7): 1.15, (8): 1.29, (9): 1.43, (10): 1.58, (11): 1.72, (12): 1.86, (13): 2.01, (14): 2.1, (15): 2.3, (16): 2.59, (17): 3.0, (18): 3.45.



A



**Fig. 9: Plots of absorbance vs. mole ratio for [macrocycle (L')] / [DDQ] in  $\text{CHCl}_3$  solution at  $33^\circ\text{C}$  and, (A) at 351 and 372 nm and (B) at 390 and 435 nm.**

The plot of absorbance vs. macrocycle (L)/DDQ mole ratio at 350 nm and some other wavelengths are shown in Fig. 9. It is quite obvious that macrocycle forms two kinds of complexes with DDQ,  $\text{L}'\text{-DDQ}$  and  $\text{L}'_2\text{-DDQ}$  forms. Such spectral features are in agreement with those reported for  $\text{DDQ}^{\bullet-}$  radical ion <sup>18,24-26</sup>.

The NMR and IR studies showed similar behavior to macrocycle (L) and confirmed the formation of complexes details are listed in Tables 5 and 6.

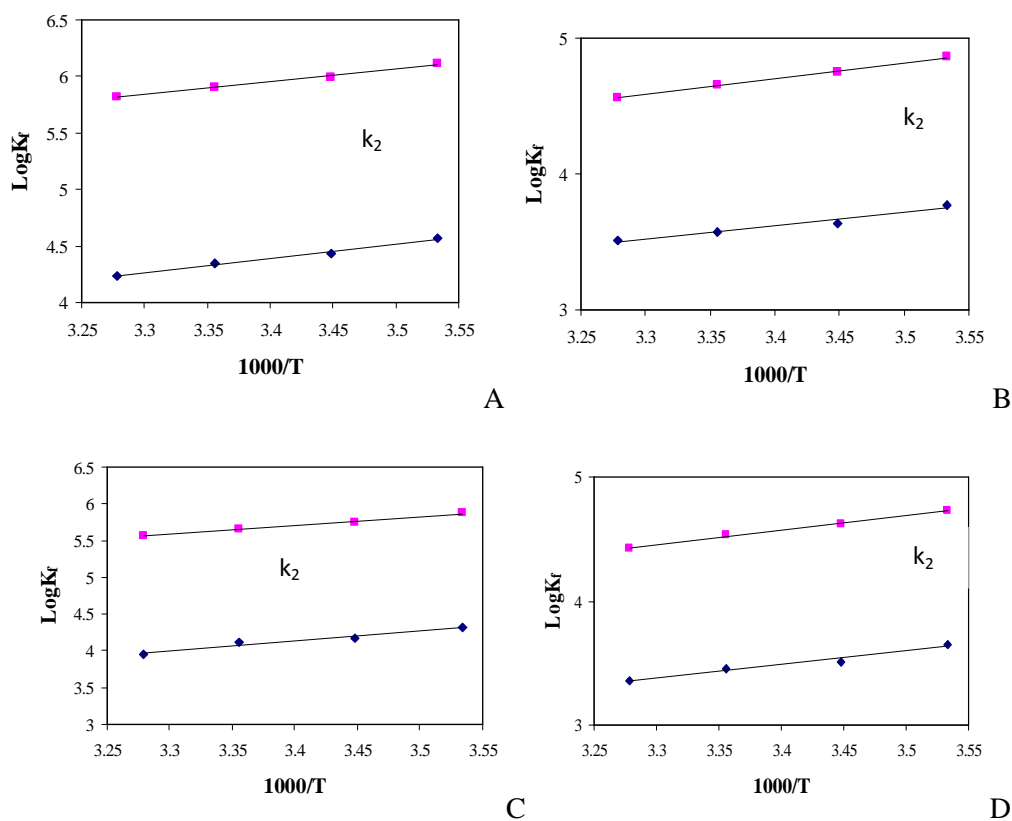
The formation constants of the resulting complexes at various temperatures were determined by use of a nonlinear, least squares, curve fitting program KINFIT, that previously described. The computer fitted curve for charge transfer complexation of macrocycle (L') with DDQ not included but the corresponding formation constants are listed in Tables 2 and 3.

In order to have a better understanding of the thermodynamic of the charge-transfer complexation reaction, it is useful to consider the enthalpic and entropic contributions of the reaction. The  $\Delta\text{H}^\circ$  and  $\Delta\text{S}^\circ$  values for the complexation reaction were evaluated from the temperature dependence of  $K_f$  by applying a linear least-squares analysis according to the Van't Hoff equation:

$$2.303 \log K_f = -\frac{\Delta\text{H}^\circ}{RT} + \frac{\Delta\text{S}^\circ}{R}$$

Thus, the  $\Delta\text{H}^\circ$  and  $\Delta\text{S}^\circ$  values were evaluated in the usual manner from the slope and intercept of the resulting linear plot of  $\log K_f$  vs.  $1/T$  (Figure 10), and the results are also included in Tables 2 and 3.

The data given in Tables 2 and 3 revealed that all of the iodine and DDQ complexes are both enthalpic and entropic stabilized. The existing such effect between  $\Delta\text{H}^\circ$  and  $\Delta\text{S}^\circ$  values, which is frequently observed for a variety of metal-ligands and charge transfer complexes, would cause overall change in the complex stability ( $\Delta\text{G}^\circ$ ) to be greater than might be expected from the change in either  $\Delta\text{H}^\circ$  or  $\Delta\text{S}^\circ$  independently.



**Fig. 10:** Van't Hoff plots for A) macrocycle(L)-I<sub>2</sub> B) macrocycle(L)-DDQ C) macrocycle(L')-I<sub>2</sub> D) macrocycle(L')-DDQ in chloroform solution.

**Table 2:** Formation constants,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  values (at 25°C) for macrocycle (L) with I<sub>2</sub> and DDQ complexes in chloroform at various temperatures.

Temp. (°C)	$\log K_f$ (I <sub>2</sub> -L)	$\log K_f$ (I <sub>2</sub> -L <sub>2</sub> )	$\log K_f$ (DDQ-L)	$\log K_f$ (DDQ-L <sub>2</sub> )
10	$4.57 \pm 0.02$	$6.12 \pm 0.02$	$3.77 \pm 0.02$	$4.86 \pm 0.01$
17	$4.43 \pm 0.03$	$5.99 \pm 0.02$	$3.64 \pm 0.03$	$4.75 \pm 0.03$
25	$4.35 \pm 0.02$	$5.91 \pm 0.02$	$3.57 \pm 0.02$	$4.66 \pm 0.02$
32	$4.25 \pm 0.02$	$5.82 \pm 0.02$	$3.51 \pm 0.01$	$4.56 \pm 0.02$
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$-23.2 \pm 0.1$	$-21.9 \pm 0.2$	$-19.0 \pm 0.1$	$-22.1 \pm 0.3$
$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$5.3 \pm 2$	$40 \pm 4$	$4.7 \pm 2$	$15 \pm 5$
$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$-24.6 \pm 0.1$	$-32.7 \pm 0.2$	$-20.3 \pm 0.1$	$-26.1 \pm 0.3$

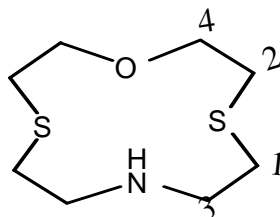
**Table-3: Formation constants,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  values (at 25°C), for macrocycle(L') with I<sub>2</sub> and DDQ complexes in chloroform solution at various temperatures.**

Temp. (°C)	log K <sub>f</sub> (I <sub>2</sub> -L)	log K <sub>f</sub> (I <sub>2</sub> -L <sub>2</sub> )	log K <sub>f</sub> (DDQ-L)	log K <sub>f</sub> (DDQ-L <sub>2</sub> )
10	4.32 ± 0.02	5.87 ± 0.02	3.65 ± 0.02	4.72 ± 0.01
17	4.18 ± 0.03	5.74 ± 0.02	3.51 ± 0.03	4.62 ± 0.03
25	4.11 ± 0.02	5.66 ± 0.02	3.45 ± 0.02	4.53 ± 0.02
32	3.96 ± 0.02	5.57 ± 0.02	3.36 ± 0.02	4.42 ± 0.02
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	-25.9 ± 0.2	-21.9 ± 0.3	-20.7 ± 0.1	-22.1 ± 0.2
$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	7.7 ± 2	34.8 ± 1	3.7 ± 2	12.5 ± 3
$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	-27.6 ± 0.2	-31.4 ± 0.3	-21.8 ± 0.1	-25.5 ± 0.2

The melting points for L (i.e. macrocycle(L) ), L(DDQ) and L<sub>2</sub>(DDQ) are respectively: (62, 86 and 113-116 °C).

As it is seen from Tables 2 and 3 in all cases L<sub>2</sub>A complexes are more stable than LA. The reason for this evidence may due to structure of the complexes, the A (ie. acceptor) is in a plane out of the molecule plate and is not placed in the hole of the crown, thus minimum energy and more stable complexes are formed when the acceptor is surrounded by two ligands and L<sub>2</sub>A are formed and in LA form acceptor cannot make stable complexes.

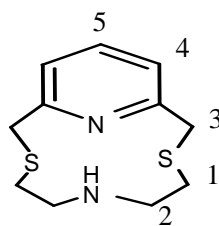
The evaluated results for NMR and IR spectroscopies are directed in Tables 4-7.



macrocycle (L)

**Table-4: <sup>1</sup>H NMR spectral data for macrocycle (L), and its complexes with I<sub>2</sub> and DDQ in CDCl<sub>3</sub>.**

[macrocycle(L)]/[I <sub>2</sub> ]	Species	$\delta$ (ppm)			
		1	2	3	4
0	L	2.72	2.75	2.8	3.58
1.0	LA	2.9	3.18	3.4	3.75
2.0	L <sub>2</sub> A	2.85	3.1	3.2	3.5
[macrocycle(L)]/[DDQ]	L				
0		2.72	2.75	2.8	3.58
1.0	LA	2.9	3.12	3.32	3.75
2.0	L <sub>2</sub> A	2.85	3.08	3.28	3.72



(L')

**Table-5:**  $^1\text{H}$  NMR spectral data for macrocycle (L'), and its complexes with  $\text{I}_2$  and DDQ in  $\text{CDCl}_3$ .

[macrocycle(L')]/[ $\text{I}_2$ ]	Species	$\delta$ (ppm)				
		1	2	3	4	5
0	L'	2.86	3.22	4.33	4.41	7.99
1.0	L'A	2.98	3.51	4.3	4.40	7.98
2.0	L <sub>2</sub> A	2.89	3.34	4.6	4.42	7.97
[macrocycle(L')]/[DDQ]	L'					
		2.86	3.22	4.33	4.41	7.99
0	L'	2.99	3.50	4.31	4.40	7.98
1.0	L'A					
2.0	L <sub>2</sub> A	2.88	3.35	4.61	4.42	7.97

**Table- 6:** IR spectral data for macrocycles and, their complexes with  $\text{I}_2$ .

[L]/[ $\text{I}_2$ ]	species	$\nu(\text{Cm}^{-1})$				
		L			L'	
		S-CH <sub>2</sub> -	N-CH <sub>2</sub> -	O-CH <sub>2</sub> -	S-CH <sub>2</sub> -	N-CH <sub>2</sub> -
0	L	2880 (s)	2700 (w)	1445 (s-sh)	2910 (m)	2750 (w)
1.0	LA	2998	-	1410	2920.1	2754.26
2.0	L <sub>2</sub> A	3000	2850	1415	2919.6	2755.4

**Table- 7:** IR spectral data for macrocycles and, their complexes with DDQ.

[L]/[DDQ]	species	$\nu(\text{Cm}^{-1})$				
		L			L'	
		S-CH <sub>2</sub> -	N-CH <sub>2</sub> -	O-CH <sub>2</sub> -	S-CH <sub>2</sub> -	N-CH <sub>2</sub> -
0	L	2880 (s)	2700 (w)	1445 (s-sh)	2910 (m)	2750 (w)
1.0	LA	2900	2820	1400	2922.01	-
2.0	L <sub>2</sub> A	3000	2830	1420	2920.65	-

## CONCLUSION

In this work the interaction of two recently synthesized mixed azathia crown ether 1,7-dithia-10-aza-12-crown-4, and pyridine based mixed azathia crown ether towards two acceptors (i.e. Iodine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)) have been examined in chloroform. The KINFIT program which was applied to UV-Visible spectroscopy data obtained from monitoring the reaction between Ligands and the acceptors. Both of the acceptors, were formed the most stable complexes with these ligands. Based on the results of this study the new synthesized ligands is introduced as new active emissive probes to detect Iodine and DDQ by absorption spectroscopy either directly or after preconcentration. Therefore these ligands can be used as new active probes to detect these compounds by absorptionspectroscopy and/or can be used for preconcentration and trace analysis of these materials indifferent samples.

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