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Synthesis & cytotoxic activity of Bis (μ – chloro) bis (azobenzenyl analogue) di-palladium complexes

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ABSTRACT

A novel light emitting palladacycles-chloride-bridged complexes namely bis (azobenzenyl)-Bis (μ-chloro)- di-palladium complex molecules are synthesized by the treatment of Rod shaped liquid crystals azobenzene analogues namely 4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butyl phenyl) di-azenyl) benzoate (R_1) and 4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butyl phenyl) di-azenyl) benzoate (R_2) with bis (benzonitrile) palladium chloride (HK-1) in chloroform at room temperature and obtained palladacycles namely Bis [(E)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) respectively are characterized by TLC, LC/MS, FT–IR, NMR, and electronic spectroscopy- UV –vis spectroscopy, it reveals the spectra for Palladacycle: Bis [(E)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis- (μ–chloro)–di-palladium (HK-3) are shown three distinct bands at 252, 336.9 & 389 nm and 255, 358 and 485 nm respectively compare to two band for Rod shaped liquid crystals R_1 and R_2 and for these palladacycles (HK-2 and HK-3) and their Rod shaped Liquid crystals starting materials (R_1 and R_2) The emission spectra recorded in fluorimetry and further, it is observed that after making palladacycle it's hard to show liquid crystal property. It's because of substituents present on azobenzene core and its stability and the thermal stability studies obtained by Thermogravimetric analysis (TGA) results shows that palladacycle of (HK-3) is more stable than HK-2. Furthermore, the In -vitro cytotoxic activity against Hela Cell lines shown that HK-3 and R_2 shown better cytotoxic activity compared to other molecules such as (R_1, HK-1 and HK-2. Hence, these (HK-3) and R_2 can be used to discover bioactive molecule that may serve as lead in the development of new pharmaceutical research activities.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Applied Research in Engineering Sciences.

1. Introduction

The chemistry of Palladacycles a versatile subject of few decades old and very long standing research area of interest and is very important in traditional as well as advanced organic synthesis and catalysis [1] as well as in a broad range of potential applications in optical properties [2]. The optical properties and reactivity and of these molecules depends on cyclopalladated substrate and these properties can be tuned by selecting an anionic or neutral ligands [2]. Synthesis of palladacycles usually involves direct C—H bond activation with Pd (II) precursors, such as $PdCl_2$, $[Pd(OAC)_2]_3$ or $(PdCl_4)^{2-}$ and $PdCl_2(CH_3CN)_2$ resulting in the formation of an acetate and Chloride bridged dimeric palladacycles [2], and their derivatives with different ancillary ligands can be formed by bridge splitting reactions with donor ligands [2] or by the substitution of chlorides and acetate ligands with azides, iodides, bromides, acetylacetonates etc. [3].

Very recently Basma al Janabi et al reported [4] a finding on palladacycles–an Innovation structural rearrangement in Imine palladacycle metal ligand chemistry, Further, Gopal Dhangar et al. reported [5] palladacycle – catalysed triple Suzuki coupling strategy for the synthesis of anthracene core-based OLED emitters, Furthermore, Francisco Reigosa-Chamorro et al reported [6]. In vitro

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and In vivo effect of palladacycles: targeting A2780 ovarian carcinoma cells and modulation of angiogenesis.

In continuation to the reported work titled polar cyano/nitrile group-derived rod-shaped nematic liquid crystals [7] here, we are reporting the palladium catalysed C—H bond activation to form a two five membered cyclopalladated molecules such as palladacycle (HK-2 & HK-3) on treatment of Bis benzonitrile palladium chloride (HK1) and rod shaped liquid crystals R_1 and R_2 respectively to achieve unique thermotropic properties of liquid crystals such as higher phase transition temperature and the reduction of mesophase temperature when compared to the liquid crystal alone and these palladacycles are characterized using standard spectroscopic techniques and also their cytotoxic studies carried out against Hela cell lines using MTT assay.

2. Experimental section

2.1. Synthesis and characterization

Solvents and chemicals all are purchased from Sigma-Aldrich and Merck and are used without further purification, Bis (benzonitrile) palladium chloride (HK-1) and *bis (azobenzenyl)-Bis–(μ-chloro)- di-palladium complexes namely* (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)] -Bis-(μ–chloro)–Di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)] -Bis-(μ–chloro)–Di-palladium (HK-3) were synthesized by the combination of HK-1 and (*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate (R_1) and 4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butyl phenyl) di-azenyl) benzoate (R_2) respectively in chloroform at room temperature and purity of the compounds are checked by the thin layer chromatography (TLC) on silica gel 60 F_{254} on aluminum sheets using pure chloroform and petroleum ether (9:1) ratio as an eluent. Precipitation done with petroleum ether or methanol, target molecules obtained are HK-1, HK-2, and HK-3 are in more than 70% yield.

2.2. Chemical/Physical analysis

NMR (^{1}H & ^{13}C) spectra were done using Bruker Biospin-500 spectrophotometer and recorded at room temperature using deuterated chloroform ($CDCl_3$). Chemical shifts δ are listed relative to Tetra methyl silane. The mesophase behaviour and transition temperatures of the (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis- (μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3), R_1 and R_2 measured using a Leica (DM2700 M) optical polarising transmitted light microscope attached to a digital camera and a Mettler FP82 HT hot stage programmed by an FP90 Central Processor. The associated enthalpies were obtained from DSC-thermograms, which were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K/min^{-1}. Using chloroform HPLC, make: Shimadzu, Model: Pump: LC-10ADVp, MS: Make: Waters, Model: Micro-mass Quattro micro, Software: Mass Lynx, Version: V4.1SCN805, MS Condition: Triple Quadrupole (QqQ) MSMS and UV– Visible absorption studies were carried out using Specord 210 plus equipped with double detection and alterable spectral resolutions. Photoluminescence studies were carried out using spectrofluorometer (Hitachi F 2700) with a constant slit width of 5 nm. X-ray diffraction studies were carried out using Bruker D8 advance diffractometer equipped with Cu k alpha radiation of wavelength 0. 15406 nm. Fourier transform infrared radiation spectroscopic studies were carried out Parkin Elmer Spectrum 1000 in the mode of attenuated total reflectance.

2.3. Procedures for synthesis of starting materials

Bis (benzonitrile) palladium chloride (HK-1) and palladacycles (Bis [(*E*)-4-((4-butoxy phenyl)-di-azenyl) phenyl 4-nitrobenzoate)] -Bis-(μ–chloro)–di-palladium (HK-2) and *Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis (μ–chloro)– di-palladium (*HK-3) are as discussed below.

2.3.1. Synthesis of bis (benzonitrile) palladium chloride (HK-1)

Palladium chloride (0.5 g, 0.002819 mol) was dissolved in benzonitrile (25 mL) and are taken in 100 mL single neck Round Bottomed flask fitted with condenser and guard tube and it is heated to 100–110 °C and maintained at 100–110 °C for 20 min, cooled to 25–30 °C and diluted with petroleum ether (50 mL), stirred for 15 min and filtered the orange yellow crystals and washed with petroleum ether and dried under vacuum. Yield: 1.114 g, yield = 70.1%, Melting point is found to be 128–130 °C, absorption recorded in UV–vis spectroscopy and maximum absorption (λ_{max}) shown three bands and are observed at 255.2, 346.4, 399.2 nm and emission spectra also recorded in Fluorimetry at 410 nm.

2.3.2. Synthesis of rod shaped liquid crystals R_1 & R_2.

Synthesis of (*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate (R_1) and *4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butyl phenyl) di-azenyl) benzoate (*R_2) are prepared as reported earlier and *experimental data of R_2 is as mentioned bellow* [7].

4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butyl phenyl) di-azenyl) benzoate (R_2): Orange solid: 85%, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ H/ppm: 0.93 (6H, m), 1.37–1.93 (8H, m), 2.69 (2H, m), 4.12 (2H, t), 7.02 (4H, m), 7.17 – 7.32 (6H, m), 7.82 (2H, d), 7.92 (2H, d), 8.25 (2H, d): ^{13}C NMR (125 MHz, $CDCl_3$):171.4, 164.0, 161.2, 154.7, 151.0, 150.8, 147.0, 145.8, 140.3, 131.8, 129.0, 126.9, 124.6, 122.5, 121.7, 114.6, 113.6, 68.4, 67.8, 35.5, 34.3, 33.5, 31.1, 28.9, 25.6, 24.8, 22.3, 19.0, 13.9, 13.7. Elemental analysis calculated for $C_{34}H_{34}N_2O_5$ (Mol. Wt.: 550.64) C, 74.16; H, 6.22; N, 5.09; found C, 74.21; H, 6.23; N, 5.11 %.

2.3.3. Synthesis of palladacycle- (Bis [(E)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ–chloro)– di-palladium (HK2)

HK-1 (0.1158 g, 0.0003 mol) and R_1 (0.1108 g, 0.00027 mol) are taken in single neck 50 mL Round Bottomed flask fitted with guard tube and charged 25 mL chloroform and started stirring at 25 – 30 °C and continued stirring at same temperature for 24 h, reaction completion checked using Thin layer Chromatography (TLC) using 7:3 of chloroform: petroleum ether as mobile phase and then reaction was subjected to distillation to remove solvent to the volume around 5 mL then petroleum ether added, stirred for 15 min and crystals filtered, dried under vacuum. Yield: 0.1423 g, Yield = 70.0% and Melting point found to be at more than 170 °C undergoes decomposition and it is stored in air tight bottle. LC/MSMS: *m/z*, ES+: 1120.59: UV absorption λ_{max} are observed at 252, 336.9 and 389 nm and photoluminescence excitation recorded at 390 nm: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ H/ppm: 0.914 (6H, t), 1.5 (4H, tq), 1.75 (4H, tt), 2.84 (4H, t), 7.46 (4H, d), 7.65 (4H, d), 8.3 (4H, d), 8.78 (4H, d), 8.87 (2H, br).

2.3.4. Synthesis of palladacycle: Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3)

HK-1 (0.1372 g, 0.0003 mol) and 4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butyl phenyl) di-azenyl) benzoate (R_2) (0.1642 g, 0.00029 mol) are taken in 50 mL Round necked Flask fitted with guard tube and charged chloroform (10 mL) and started stirring at 25–30 °C and continued stirring for 24 h at 25–30 °C

and the reaction completion checked using thin layer chromatography (TLC) of 7:3 chloroform: Petroleum ether as mobile phase and solvent removed completely under vacuum and methanol (10 mL) is added and stirred for few minutes, filtered the obtained crystals and dried under vacuum. Yield: 0.1425 g and it is 71% yield and the Melting point is found to be decomposition at more than 140 °C and it is stored in air tight bottle, LC/MS MS: *m/z* ES+: 1413.23: absorption (λ_{max}) recorded in UV–vis spectroscopy and three bands are observed at 255, 358 and 485 nm and excitation recorded at 490 nm in fluorimetry: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ H/ppm: 0.89 (6H, t), 1.47–1.87 (16H, m), 2.665 (4H, t), 9.976 (4H, s), 6.97 (4H, d), 7.13 (4H, d), 7.21 (4H, d), 7.4 (4H, d), 7.6 (4H, d), 7.78 (4H, d), 7.83 (4H, m), 8.22 (2H, s): ^{13}C NMR in $CDCl_3$: 164.06, 150.76, 131.81, 126.89, 122.83, 121.71, 120.66, 113.62, 68.45, 50.86, 31.13, 19.03, 13.94, 13.70: FT-IR ATR mode transmittance in cm^{-1}: 3390, 3373, 2959, 2947, 2932, 2918, 2867, 2852, 1735, 1705, 1601, 1585, 1527, 1499, 1467, 1459, 1449, 1438, 1414, 1391, 1374, 1347, 1304, 1263, 1207, 1158, 1119, 1106, 1076, 1065, 1037, 1027, 1005, 966, 933, 966, 933, 872, 852, 827, 752, 714. 688, 668 and 640 cm^{-1}.

2.4. Cytotoxic activity

2.4.1. Cell culture and treatment

The HeLa cells were collected from the National Cell Science Centre in Pune. The cell culture growth medium was DMEM medium with 10% FBS, 100 U/mL antibiotic and antimycotic solution added. Cells were cultivated at 37 °C in a humidified incubator with 95% air and 5% CO_2. After 80% of confluency, the cells were sub-cultured by treating them for 10 min with trypsin-EDTA and then adding complete media to block the process.

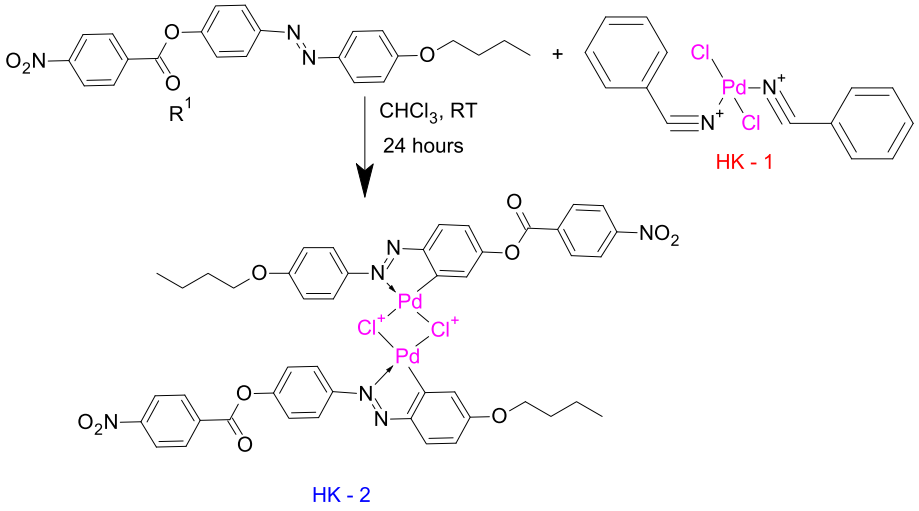

Fig. 1. Scheme for the synthesis of palladacycle – HK-2.

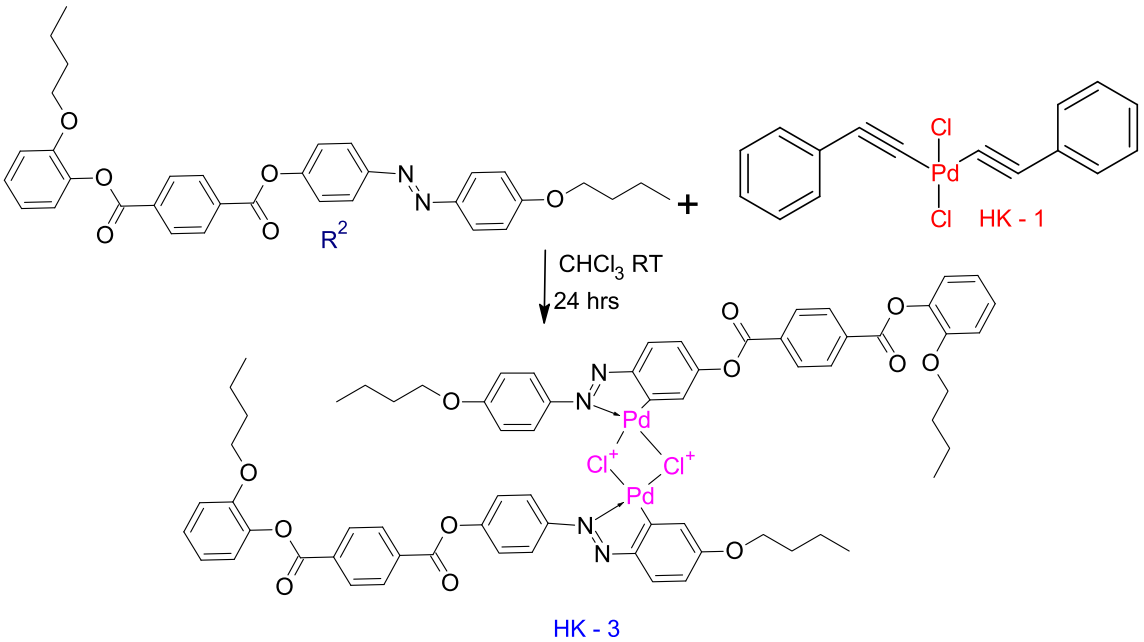

Fig. 2. Scheme for the synthesis of Palladacycle -HK-3.

2.4.2. MTT assay

The MTT reduction test was used to assess cell viability in the study described in the method of Mosmann (1983). In a 96-well micro-titre plate, HeLa cells were seeded (concentration 1×10^4 cells/mL) They were then incubated for 24 h at 37 °C and 5% CO_2 to allow them to attach to the bottom of the wells of the plate. Each R_2, HK-1 and palladacycles (HK-2 & HK-3) was made into a stock solution with a concentration of 1 mg/mL before being added to the micro-titre plate. Each R_1, R_2, HK-1 and Palladacycles (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) was serially diluted to a concentration ranging from 2.5 g/mL to 250 g/mL, an additional 24 h were spent incubating the micro-titre plate. 2% DMSO-exposed vehicle-treated cells were present in the control wells. MTT (5 mg/mL) was incubated in cells for 4 h. The absorbance was measured at 570 nm after the DMSO was used to solubilize the dark blue formazan crystals that formed in living cells. With the help of an ELISA Plate reader (Mode Tecan 1650), the absorption was assessed. Results were presented as a percentage MTT reduction in comparison to control cell absorbance.

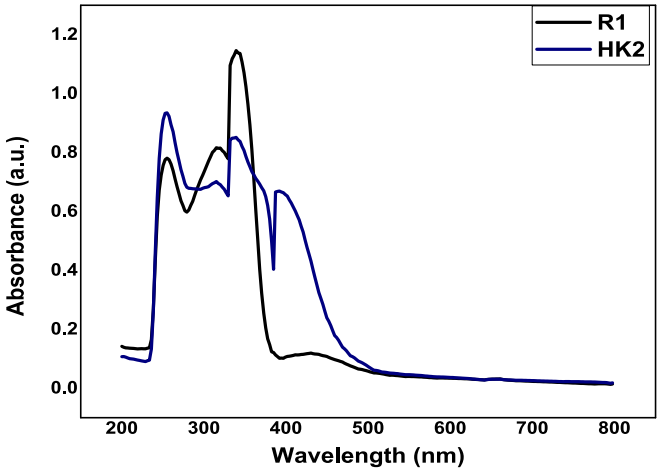

Fig. 3. UV –vis spectra of HK-2 and rod-shaped liquid crystal R_1.

3. Results and discussion

One of the intermediate which acts as source of Palladium chloride for the formation palladacycles (HK-2 & HK-3) is bis (benzonitrile) palladium chloride (HK-1) and its synthesis involves the treatment of palladium chloride and benzonitrile and which are taken in Round bottom single necked 100 mL flask and heated the reaction mass to 110–115 °C and this temperature further maintained for 20 min, cooled and diluted with Petroleum ether and filtered the orange yellow crystal (HK-1) and dried under vacuum and which is used to synthesize light emitting palladacycles (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ –chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) on treating with R_1 and R_2 respectively, in chloroform at room temperature and these are obtained followed by workup to get (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis(μ –chloro)–Di-palladium (HK-3) and the scheme for the preparation is as follows in Figs. 1 and 2.

3.1. Electronic spectroscopy

Palladacycle synthesised (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ – chloro) – Di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) including Rod shaped liquid crystals R_1 and R_2 and Bis (Benzonitrile) palladium chloride (HK-1) have been characterized using UV–visible spectroscopy in chloroform solvent. showed distinct two peaks with respect to characteristic of azobenzene π – π* intramolecular charge transfer (ICT) transitions for azobenzene analogues such as Rod -shaped Liquid crystal (R_1) absorption spec-

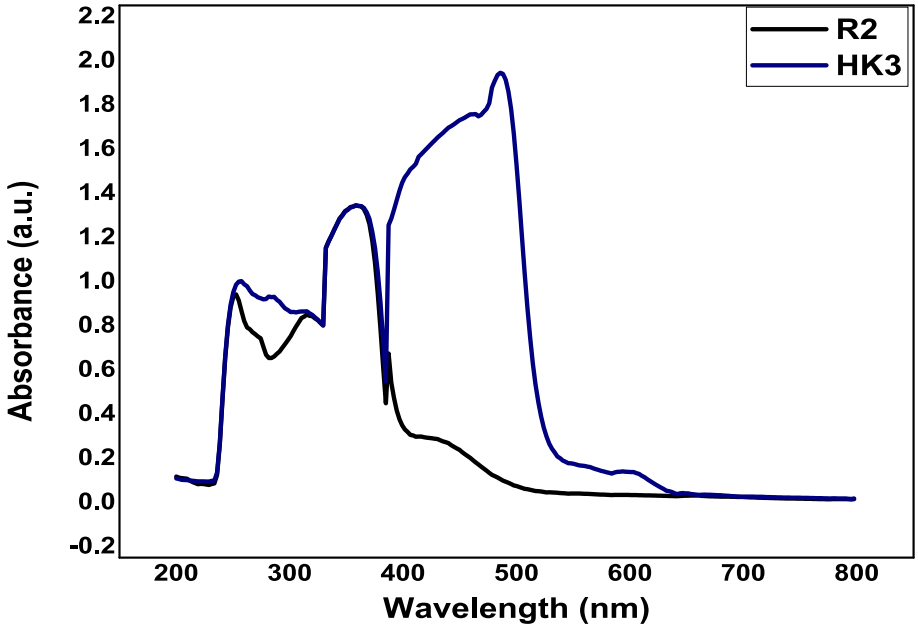

Fig. 4. UV – vis Spectra of palladacycle -HK-3 and rod-shaped liquid crystal-R_2.

trum (λ_{max}) which is a starting material for the synthesis of palladacycle (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitro benzoate)]-Bis-(μ–chloro)– di-palladium (HK-2) is compared with the absorption spectra of HK-2 and it is as shown in Fig. 3.

And the starting material (*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate (R_1) has shown two distinct peaks at 252.8 and 339.2 nm while the Palladacycle (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis- (μ–chloro)–di-palladium (HK-2) showed three peaks at 252, 336.9 & 389 nm. A peak at 389 nm indicates the formation of Palladacycle complex and here noted one result is about enhanced absorption for HK-2 observed to compare with Rod shaped Liquid crystal starting material (R_1) and HK-1 whereas the absorption of the starting material (R_1) was limited to the UV region.

Almost the same optical property is obtained in the case of Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) also as shown in Fig. 4 and the Rod- shaped Liquid crystal starting material R_2 UV –visible absorption (λ_{max}) observed at 250, and 356 nm. But for the palladacycle (HK-3) evidenced an enhanced absorption around 485 nm in addition to 255 & 358 nm ones. The analysis of the optical absorption property of (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) implies that these palladacycles in general exhibits enhanced visible light absorption compared to their rod shaped liquid crystal starting materials result from the increased electronic asymmetry caused by the presence of electrons of d as shown in the Fig. 5.

The photoluminescence emission spectrum of the starting material HK-1 and rod-shaped liquid crystals (*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate (R_1) was compared with the palladacycle (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl)

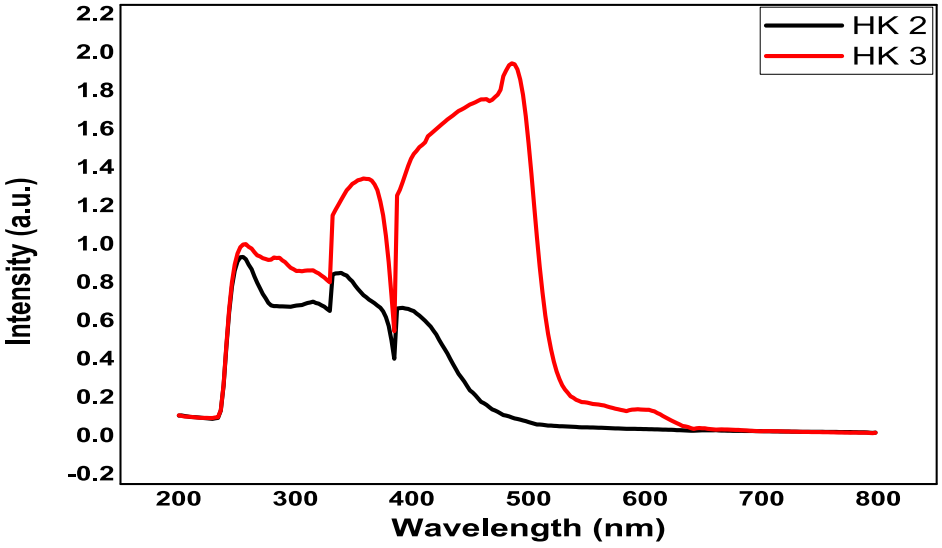

Fig. 5. UV – vis spectra of palladacycles HK-2 and HK-3.

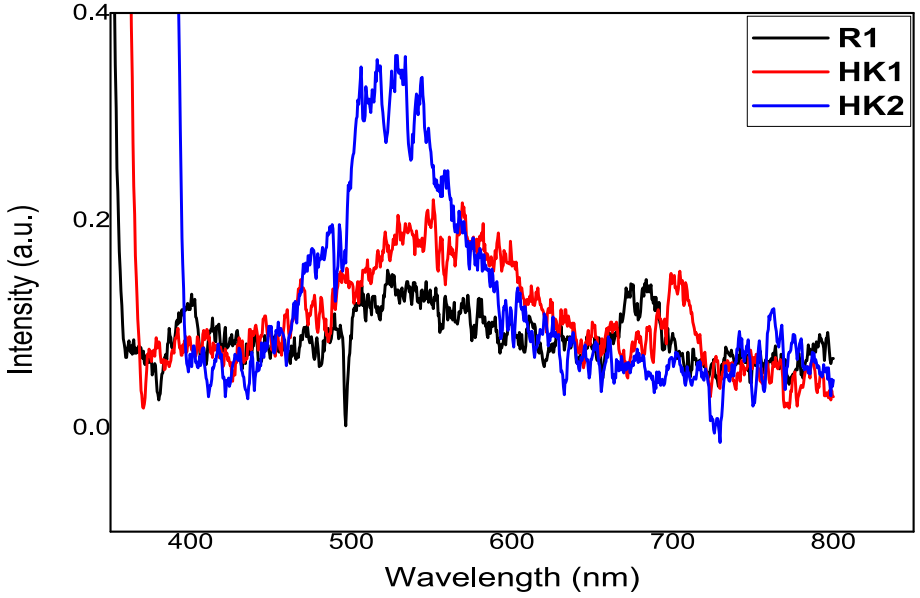

Fig. 6. Photoluminescence emission spectra of HK-1 & palladacycle -HK-2 comparison with rod shaped liquid crystal R_1.

phenyl 4-nitrobenzoate)]-Bis-(μ–chloro)–Di-palladium (HK-2) as shown in Fig. 6.

The nature of the emission spectra of HK-2 is comparable with parent liquid crystal and HK-1. But the intensity of Photoluminescence emission observed in HK-2 is comparatively very high with respect to the rod-shaped liquid crystals (R_1) starting materials. The maximum emission intensity is observed at a wavelength of 550 nm.

The photoluminescence emission spectra of Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) compared with HK-1 and R_2 as shown in Fig. 7.

Though the nature of Photoluminescence emission spectra of palladacycles HK-1 and HK-3 are comparable, the intensity of HK-3 is comparatively less with respect to HK-1 and R_2. This is probably due to the internal energy transfer occurred during the formation of palladium complex that resulted in the quenching of photoluminescence emission.

In addition, to further probe the effects of on the thermal stability, the Thermo gravimetric Analysis (TGA) is useful tool for analysing the thermal stability of the palladacycles (HK-2 & HK-3) in recent year this tool has been applied to molecules with possible OLED applications because of the thermal stability and the TGA curves of palladacycles (HK-2 & HK-3) represented as in Fig. 8.

These two palladacycles bear the identical n – butyl oxy group at the one end of the terminal side and the other end differ by nitro-benzoyl group in HK-2 & Ter-phthalyl group in HK-3 and the Thermo-gravimetric analysis (TGA) curves does not show similarity in degradation curves. To be particularly, the weight loss started approximately between 200 °C and 250 °C and the 100% loss occurs between 400 and 900 °C. In the case of HK-3 and it shows that higher thermal stability.

3.2. Cytotoxicity studies

Cytotoxicity of Pro – ligands *(E)-4-((4-butoxy phenyl)di-azenyl) phenyl 4-nitrobenzoate* (R_1), *4-((2-butoxy phenoxy) carbonyl) phenyl (E)-4-((4-butyl phenyl) di-azenyl) benzoate* (R_2), HK-1, and Palladacycle (Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitro benzoate)]-Bis-(μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) are discussed.

Palladacycles (HK-2 and HK-3) and their starting materials such as HK-1, and R_1, R_2 materials biological assay were evaluated using the MTT colorimetric assay for their anticancer activities. The HK-1, palladacycles (Bis [(*E*)-4-((4-butoxy phenyl)-di-azenyl)-phenyl-4-nitrobenzoate)]-Bis-(μ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(μ–chloro)–di-palladium (HK-3) and (*E*)-4-((4-butoxy phenyl)di-azenyl) phenyl 4-nitrobenzoate (R_1), R_2 were tested for their potential to kill HeLa cells in vitro. and IC_{50} values were determined. Palladacycle HK-3 and their starting material R_2 strongly restricted the growth of HeLa cells as shown in Fig. 9 and with IC_{50} values 98.6 μg/mL and 96.23 μg/mL, respectively and Fig. 10 shows the antiproliferative activity of HK-1, HK-2, HK-3, R_1 & R_2 against HeLa cells and further, the HK-1 did not have any effect on the cells.

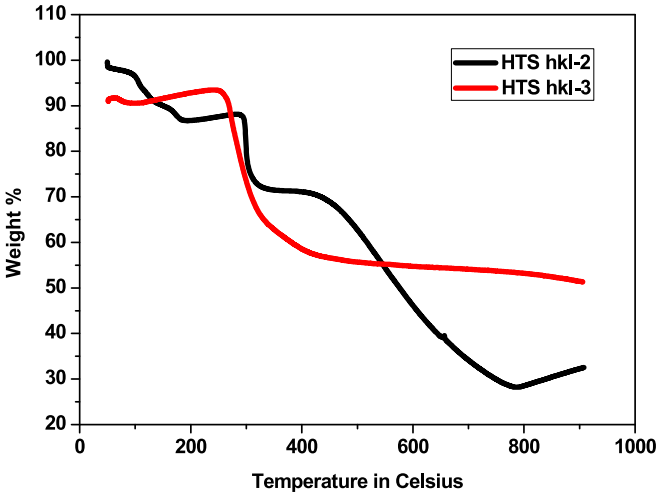

Fig. 8. Thermogravimetric analysis (TGA) of palladacycles- HK –2 & HK-3.

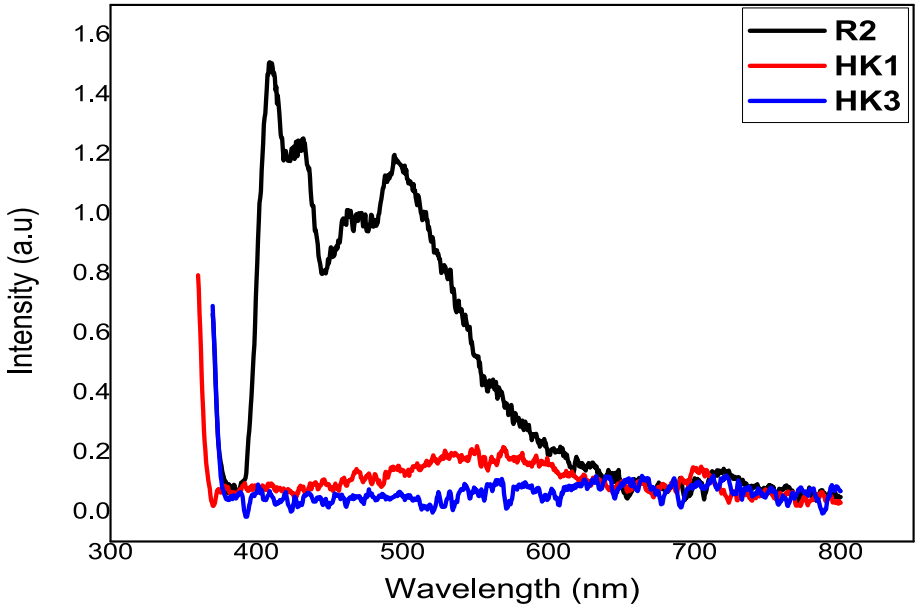

Fig. 7. Photoluminescence of emission spectra of HK –1 & Palladacycle- HK-3 comparison with rod-shaped liquid crystal R_2.

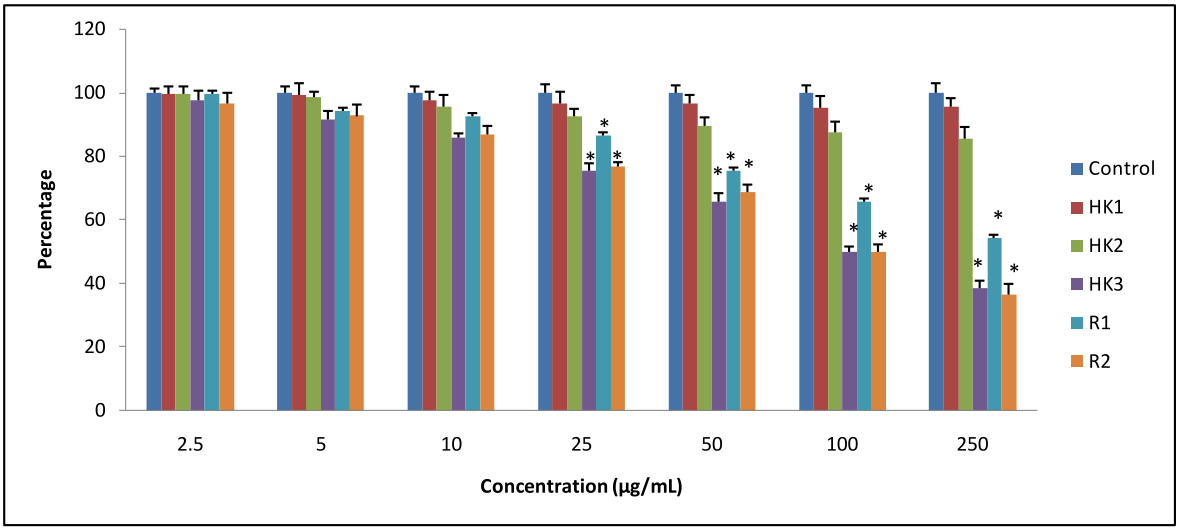

Fig. 9. Anti-cancerous effects of HK-1, HK-2, HK-3, R_1 and R_2 against HeLa cells. The data are analyzed by one-way ANOVA followed by Tukey's test and is expressed a mean ± SE from six independent experiments. *$p < 0.05$, compared with control.

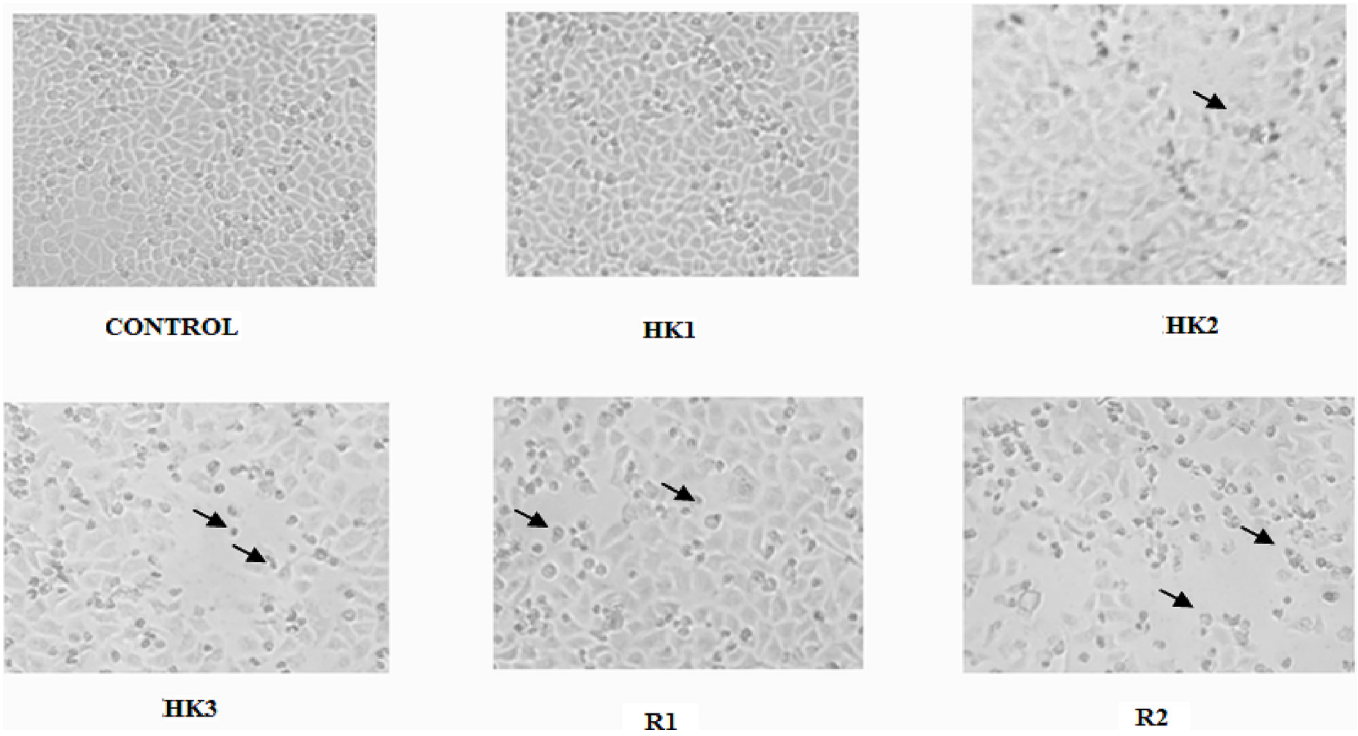

Fig. 10. Anti-proliferative effects of HK-1, palladacycles- HK-2, HK-3 and rod-shaped liquid crystals- R_1 and R_2 (100 µg/mL) against HeLa cells (→indicates dead cells with shrunken cell bodies).

4. Conclusions

A novel light emitting palladacycles-chloride-bridged complexes namely bis (azobenzenyl)-Bis-(µ-chloro)- di-palladium molecules were synthesized by the treatment of Rod shaped liquid crystal azobenzene analogues namely 4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butyl phenyl) di-azenyl) benzoate (R_1) and 4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butyl phenyl) di-azenyl) benzoate (R_2) and bis (benzonitrile) palladium chloride (HK-1) in chloroform at room temperature and the isolated palladacycles Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(µ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)-Bis-(µ–chloro)–di-palladium (HK-3) molecules are characterized by using TLC, LC/MS, FT-IR, NMR and electronic spectroscopy- UV vis- spectroscopy and it reveals the spectra for Palladacycle: Bis [(*E*)-4-((4-butoxy phenyl) di-azenyl) phenyl 4-nitrobenzoate)]-Bis-(µ–chloro)–di-palladium (HK-2) and Bis [(4-((2-butoxy phenoxy) carbonyl) phenyl (*E*)-4-((4-butylphenyl) di-azenyl) benzoate)]-Bis-(µ–chloro)–di-palladium (HK-3) three distinct bands at 252, 336.9 & 389 nm and 255, 358 and 485 nm respectively and also for these palladacycles (HK-2 and HK-3) and their starting materials (R_1 and R_2) The emission spectra recorded in fluorimetry and further, it is observed that after mak-

ing palladacycle it's hard to show liquid crystal property and this is because of substituents present on HK-2 & HK-3 and their stability And the thermal stability obtained by Thermogravimetric analysis (TGA) results shows that palladacycle of (HK-3) is more stable than HK-2 because of Ter-phthalyl and alkyl group o either side of azobenzene. Furthermore, the In -vitro cytotoxic activity of palladacycle (HK-2 & HK-3) against Hela Cell lines shown that HK-3 and R_2 shown better active compared to other molecules such as (R_1), HK-1 and HK-2 against Hela Cell lines. Hence, these (HK-3) and R_2 can be used to discover bioactive molecule that may serve as lead in the development of new pharmaceutical research activities.

CRediT authorship contribution statement

P. Hareesh Kumar: . **Nagaraju Kottam:** Data curation. **R. Sowbhagya:** Formal analysis.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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