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Synthesis and charactarization of nematic palladio mesogenic molecules: Bis (μ-chloro)-bis (azobenzenyl analogue) di-palladium complexes

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Nematic palladio mesogenic molecules are synthesized and characterized by UV-visible spectroscopy, FT-IR, LC/MS, NMR, thermogravimetric analysis (TGA) and photoluminescence studies. UV-vis spectroscopy reveals the spectra that displayed three distinct bands for bis[((*E*)-1-(4-((8-bromooctyl)oxy)phenyl)-2-(4-butylphenyl)diazene)]- bis (μ-chloro)-di-palladium complex (HK-2) and bis [*E*)-1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-nitrophenyl)diazene]-bis(μ-chloro)-di-palladium complex (HK-3) and the λ_{max} values observed at 246.8, 366.7, 458.5 and 256.4, 398, 500.3 respectively. The molecules HK-2 and HK-3 exhibit a unique thermal property achieving higher phase transition temperatures and the reduction of mesophase temperature range as compare to that of the starting materials alone.

Keywords: Synthesis, Nematic, Liquid crystal, Palladio mesogenic molecules, Palladacycle

The synthesis of Palladio mesogenic molecules centers on the chemistry of organopalladium (II) complexes, a dynamic and widely studied area that has garnered interest over the past several decades. These complexes are among the most accessible and straight forward to prepare within the realm of transition metal chemistry. The foundational work in this field began in the mid 1960s, when Cope and Co-workers successfully isolated and characterized organopalladium(II) complexes incorporating azobenzene derivatives, making a pivotal moment in the development of this research domain[1,2]. Since the initial studies on azobenzene based organopalladium(II) complexes, extensive research has explored a wide array of alternative donor groups, these include Imines[3,4], pyridines[5,6], thioketones[7], amides[8-10], amidines[8], oxazolines, ligands containing phosphorous and arsine (III) containing ligands[11], as well as thioethers[12], and ethers Many chloro-bridged dimeric palladacycles have been synthesized using tertiary amines and imines favoured for their ability to form stable five or six membered metallocyclic rings[13,14]. Di-nuclear cyclopalladated complexes of the type $[(C^{\wedge}N)Pd(\mu\text{-}Cl)]_2$containing azobenzene molecules were synthesized by the reaction of $M_2[PdCl_4]$(where M = Li or K) with aromatic C- H substrates featuring a planar sp^2-Nitrogen atom[15-17]. Ghedini and co-workers were the first to report the X-ray crystal structure of di-μ-chloro-bis[(2', 6'-dimethylazobenzenato-C2^N2)-palladium (II)] [19]. structural analysis revealed that the two [(C^N) Pd moieties are nearly coplanar. Forming a distinctive a H-shaped molecular geometry[18,19]. The identity of the bridging halides, μ-Cl, Br and I plays a crucial role in influencing the phase behaviour and transition temperatures of the complexes[20-22]. The chloro-bridged complex featuring four aliphatic chains displayed an atypical mesomorphic phase progression at elevated temperatures, transitioning from a highly ordered crystalline C phase to the disordered nematic [N] phase, followed by the emergence of an ordered smectic E mesophase, and ultimately culminating in an isotropic liquid state[21-22]. These di-nuclear cyclopalladated complexes of the type $[(C^{\wedge}N)\ Pd\ (\mu\text{-}Cl)]_2$, incorporating azobenzene with extended hydrocarbon chains, have been identified as nematic palladio mesogenic molecules. They display distinctive thermal behaviour, characterized by elevated phase transition temperatures and a narrowed mesophase temperature range compared to their corresponding liquid crystalline ligands. In a recent development, Espinet and co-workers reported a series of imine based dimeric palladacycles[23].

The ever-growing LCs emanating from conventional and non-conventional system to find applications in various electronic appliances. In

continuation to our previous reported work[24], here we reporting novel nematic liquid crystal Bis-(μ-chloro)-bis-(azobenzenyl analogues)-di-palladium complexes and further, these are characterized and their liquid crystal studies determined.

Experimental Section

Synthesis and characterization

All chemicals and solvents are purchased from Merck, Sigma-Aldrich and Lobachem and used without further purification, all precursor molecules and the target molecular structure designs HK-1, HK-2 and HK-3 were easily prepared. Progress of the reaction and purity of the compounds were verified by the thin layer chromatography 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 and methanol and target molecules obtained HK-1, HK-2 and HK-3are in 70-80% yield. Purification of the palladio mesogenic molecules are verified using TLC in chloroform as a mobile phase. Molecular mass was confirmed by Mass Spectrometer using Waters, Model: Micromass Quattro micro, Software: Mass Lynx, Version: V4.1SCN805, MS Condition: Triple Quadrupole (QqQ) MSMS.

Chemical structure is confirmed by Nuclear Magnetic Resonance (NMR) spectroscopy using Bruker Biospin model; Ascent 500 instrument. Chemical shifts δ are listed relative to Tetra methyl silane $Si(CH_3)_4$ using the signal of the deuterated solvent as internal reference (δ 7.26 and 77.0 for ^1H and ^{13}C, respectively) standard. Resonance multiples are indicated as s (singlet), d (doublet), t (triplet), qt (quintet), dd (doublet of doublet), qr (quartet), m (multiplet). The mesophase behaviour and transition temperatures of the palladio mesogenic molecules, 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}.X-ray diffraction studies were carried out using Bruker D8 advance diffractometer equipped with Cu-kα radiation of wavelength 0.15406 nm. Fourier transform infrared radiation spectroscopic studies were carried out using Parkin Elmer Spectrum 1000 in the mode of attenuated total reflectance.

Procedure for the synthesis of starting materials that is the initial rod-shaped liquid crystalline with terminal alkyl bromide derivatives HK-2 sm (starting material) and HK-3sm (starting material) were prepared according the literature reported[25] and their Palladio-mesogenic molecules (HK-2 and HK-3) preparation is discussed as follows.

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

Palladium chloride (0.5g, 0.0028 mol) was dissolved in benzonitrile (25 mL, 0.2496 mol) in single necked round bottom flask and fitted with condenser and guard tube and it is heated to 110-110°C and maintained at 100-110°C for 20 min, cooled, diluted with petroleum ether (25 mL) and filtered. The orange yellow crystals was washed with petroleum ether and dried under vacuum. Yield: 0.9734g, Melting Point: 129-130°C, recorded absorbance in chloroform in UV-vis spectroscopy and maximum absorption λ_{max} are observed at 255.2, 346.4, 399.2 nm and also emission spectra recorded in Fluorimetry at 410 nm wave length.

Synthesis of palladio mesogenic molecule[((E)-1-(4-((8-bromo-octyl)-oxy)-phenyl)-2-(4-butylphenyl)diazene)]- bis (μ-chloro)-di-palladium complex (HK-2):

Bis (benzonitrile) palladium chloride (HK-1) (0.2161g, 0.00056 mol) and [((*E*)-1-(4-((8-bromooctyl)oxy)phenyl)-2-(4-butylphenyl)diazene)] (HK-2sm) (0.2161g, 0.00051 mol) are taken in single neck 50 mL round bottomed flask and charged chloroform (25 mL) and started stirring and continued stirring for 14 hours, checked TLC using 8:2 of chloroform: petroleum ether as mobile phase and the reaction was subjected to distillation up to the total volume around 2 mL and ethanol (10 mL) is added, stirred for 15 min and filtered, dried under vacuum. Yield 0.4553 g (80.0%) solid. m.p. <>114°C it undergoes decomposition. LC/MSMS: *m/z* ES: 1173.03; UV absorption λ_{max} are observed at 246.8, 366.7 and 458.5 nm and photoluminescence excitation spectra recorded at 460 nm; ^1H NMR ($CDCl_3$): δ_H 1.035 (3H, t), 1.376-1.508 (20H, m), 1.624 (2H, tt), 1.635 (2H, tt), 1.808 (2H, tt), 1.867 (2H, tt), 2.612 (2H, t), 2.682 (2H, t), 3.714 (2H, t), 3.727 (2H, t), 4.041 (4H, s), 6.7 (2H, d), 6.82 (2H, d), 6.88 (2H, d), 6.97 (2H, d), 7.56 (2H, d), 7.7 (2H, d), 7.8 (2H, d), 8.2 (2H, br).

Synthesis of palladio mesogenic molecule Bis [E)-1-(4-((6-bromo-hexyl)-oxy)phenyl)-2-(4-nitrophenyl) diazene]-Bis(μ-chloro)-di-palladium complex (HK-3):

Bis (benzonitrile) palladium chloride (HK-1) (0.1038g, 0.00027 mol) and (*E*)-1-(4-(6-bromo hexyl

oxy) phenyl)-2-(4-nitro phenyl) diazene(HK-3sm) (0.1g, 0.00024 mol) are taken in single neck 50 mL round bottomed flask and charged chloroform (25 mL) and started stirring and continued stirring for 24 h at 25-30°C and checked TLC using 8:2 of chloroform: petroleum ether and the reaction was subjected to distillation of volume around 2 mL and petroleum ether added and decanted and ethanol (10 mL) added, stirred for 15 min and filtered, dried under vacuum. Yield 0.2155 g (80%). m.p. <>124°C undergoes decomposition. LC/MSMS: *m/z* ES: 1095.49; UV absorption λ_{max} are observed at 256.4, 398 and 500.3 nm and photoluminescence excitation recorded at 500 nm; FT-IR ATR mode transmittance: 1700, 1582, 1520, 1472, 1453, 1334, 1262, 1238, 1200, 1167, 1151, 1136, 1109, 1025, 1010, 1003, 989, 962, 940, 885, 854, 821, 800, 765, 750, 731, 708, 674, 654, 637, 617 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.241 (4H, t), 1.534 (2H, tt), 1.569 (2H, tt), 1.623 (2H, t), 1.696 (2H, tt), 1.881 (2H, tt), 1.954 (2H, tt), 3.712 (2H, t), 3.725 (2H, t), 4.089 (2H, s), 4.2 (2H, s) 6.78 (2H, d), 7.16 (2H, d), 7.8 (2H, d), 7.96 (2H, d), 8.02 (2H, d), 8.12 (2H, d), 8.42 (2H, s); ^{13}C NMR: δ 160.61, 149.67, 145.61, 130.95, 128.79, 128.70, 128.39, 126.41, 125.60, 125.48, 124.92, 123.44, 115.13, 114.09, 68.53, 58.49, 35.49, 33.96, 33.36, 33.20, 32.78, 29.20, 29.15, 29.01, 28.70, 28.67, 28.11, 25.94, 25.86, 22.41, 22.33, 18.44, 13.95.

Results and Discussions

The synthesis of HK-1, involves the treatment of palladium chloride and benzonitrile and are taken in 100 mL single necked round necked flask and heated to 100-110°C and maintained at 110°C for 20 min, cooled, diluted with petroleum ether and filtered to obtain orange yellow crystals (HK-1) which is used to make palladiomesogenic molecules (HK-2 and HK-3) in addition with [((*E*)-1-(4-((8-bromooctyl) oxy) phenyl)-2-(4-butylphenyl)diazene)]- (HK-2sm) and [*E*)-1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-nitrophenyl) diazene] (HK-3sm) respectively, in chloroform at room temperature and followed by workup leads to palladio mesogenic molecule (HK-2 and HK-3) and the synthetic scheme is as follows in Fig. 1.

The starting materials HK-2sm and HK-3sm and their novel palladio mesogenic molecules (HK-2 and HK-3) are synthesised including bis(benzonitrile) palladium chloride (HK-1) have been characterized by UV-visible spectroscopy in chloroform solvent to compare and understand the photophysical properties. They have showed two distinct peaks with the characteristic of azobenzene π-π* intramolecular charge transfer (ICT) transitions for azobenzene analogues and here final palladio mesogenic molecules (HK-2 and HK-3) are recorded the absorbance and plotted nm against absorbance and it mentioned as in Fig. 2 and it reveals the spectra for palladio mesogenic molecule displayed three distinct bands for nematic palladio mesogenic molecule (HK-2 and HK-3) are found 246.8, 366.7, 458.5 and 256.4, 398, 500.3 nm respectively. The starting material (HK-2sm) has shown two distinct peaks at 242.7 and 351.6 and HK-3sm showed two peaks at 255 and

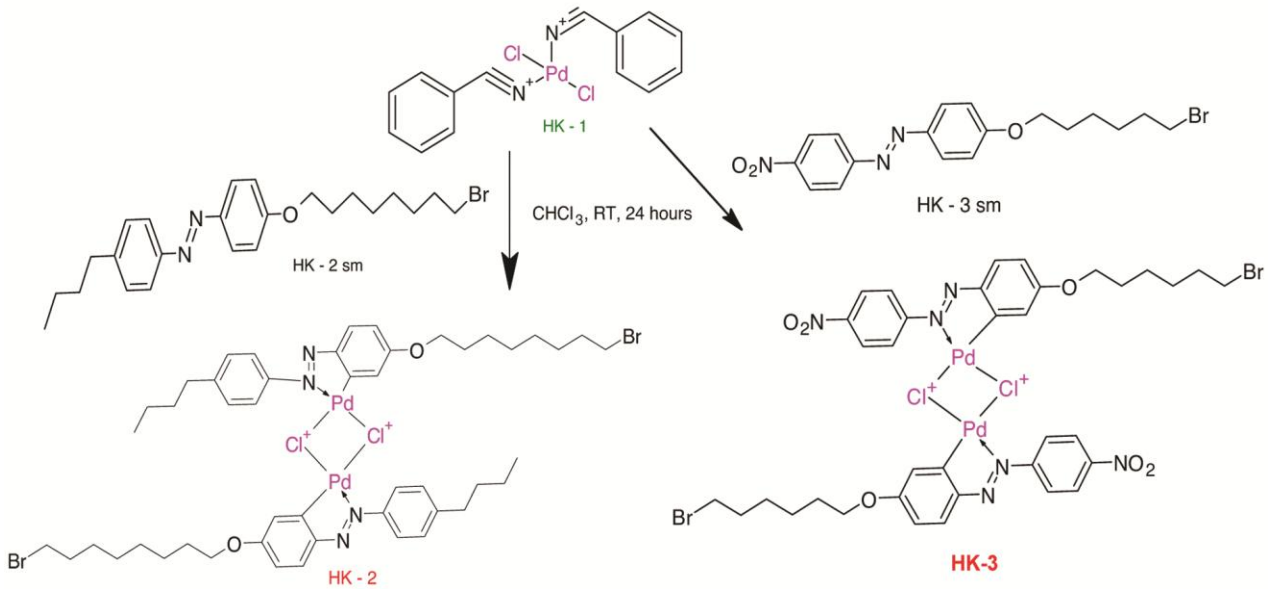


Fig. 1 — Preparation of Palladio mesogenic molecules HK-2 and HK-3

378.3 nm while the palladiomesogens HK-2 and HK-3 showed three peaks and this enhanced absorption in the visible region is because of d-electrons and whereas the absorption of the starting material was limited to the UV region as shown in Fig. 2.

The photoluminescence (PL) spectrum of present two palladiomesogenic molecules HK-2 and HK-3 was compared as shown in Fig. 3. The nature of the emission spectra of HK-2 is comparable with liquid crystal palladio complex HK-5. But the intensity of PL emission observed in HK-2 and HK-3 are comparatively very similar. The maximum emission intensity is observed at a wavelength of 430 nm as shown in Fig. 3.

Further, Differential scanning calorimetry (DSC) spectra of starting compound of HK-2 sm and DSC spectra of palladio mesogenic molecule -HK-2 are compared and also DSC spectra of compound starting molecule of HK-3sm, and DSC spectra of palladio mesogenic molecule -HK-3 are compared and it reveals the liquid crystal property and it is shown as Fig. 4.

palladiomesogenic molecules (HK-2 and HK-3) are liquid crystalline azobenzene derivatives with flexible alkyl bromide chain at one terminal end. These palladio mesogenic molecule of HK-2 and HK-3 are subjected to verify the liquid crystalline studies; both the complexes are showing interestingly liquid crystal properties. The mesophases are observed through polarised optical microscope evidenced purely nematic mesophase with mosaic and sandy

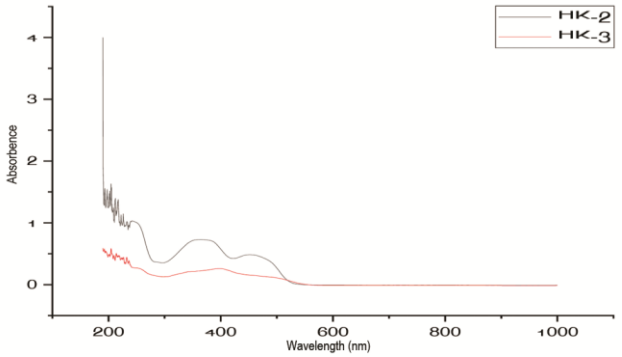


Fig. 2 — Absorbance spectra of Palladiomesogenic molecules HK-2 and HK-3

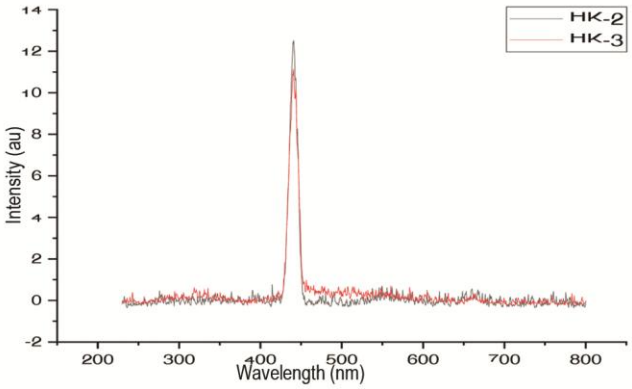


Fig. 3 — Emission spectra of Palladio mesogenic molecules HK-2 and HK-3.

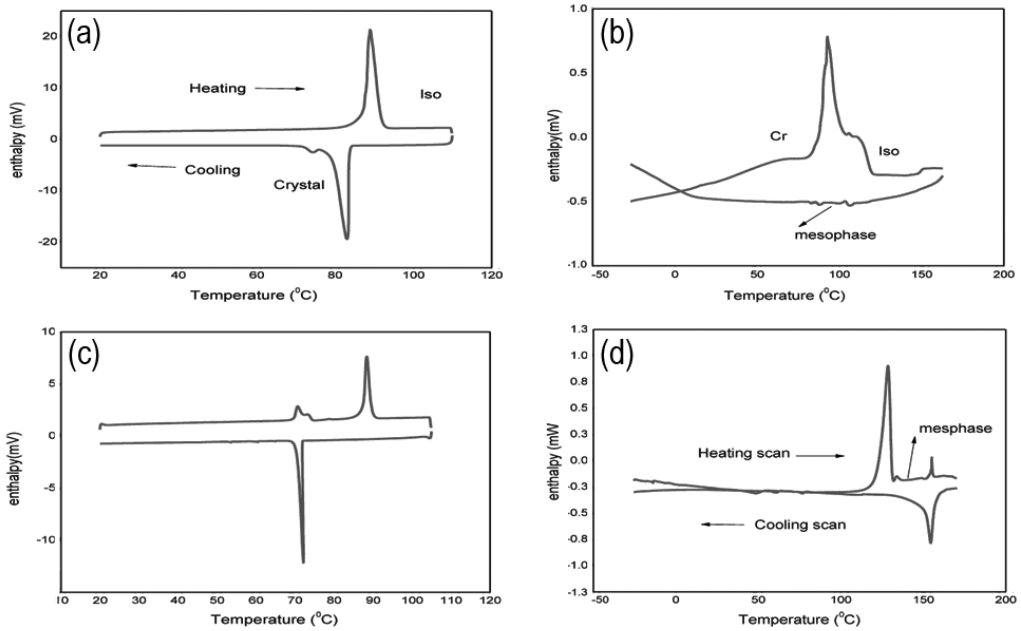


Fig. 4 — (a) Differential scanning calorimetry (DSC) spectra of starting compound of HK-2 sm, (b) DSC spectra of HK-2, (c) DSC spectra of compound starting molecule of HK-3 sm, (d) DSC spectra of HK-3.

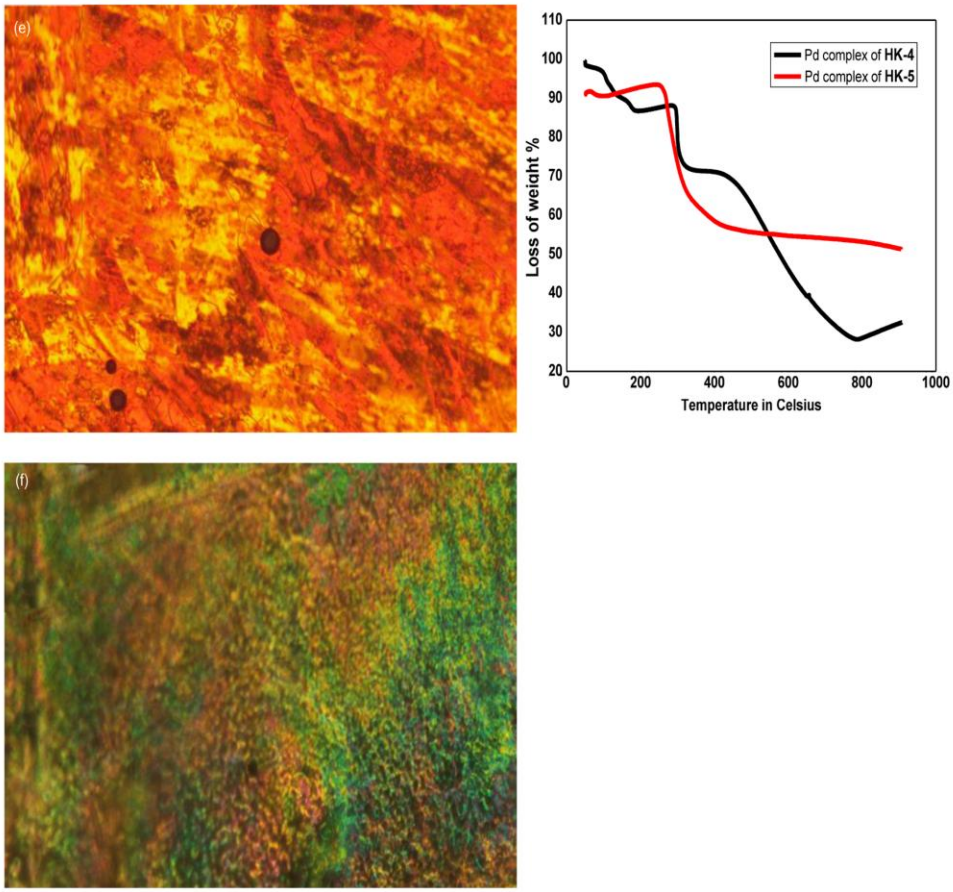


Fig. 5 — (e) Optical photomicrograph of palladiomesogenic molecules HK-2 at 100°C on cooling scan, (f) Optical photomicrograph of palladiomesogenic molecules HK-3 at 130°C on heating scan, (g) TGA curves of palladiomesogenic molecules HK-2 andHK-3.

liquid crystalline textures as shown in Fig. 5(e) and Fig. 5(f), respectively.

These nematic palladio-mesogenic molecules which exhibited a unique thermal property achieving higher phase transition temperatures and the reduction of mesophase temperature range as compare to that of the liquid crystalline ligands alone.

Thermogravimetric analysis (TGA) shows that palladio-mesogenic molecule HK-2shows three losses, whereas palladio-mesogenic molecule HK-3shows clearly a single loss. In both the palladium complexes 100% loss was not occurred due to metal retains back, only organic content was degraded. As TGA shows both the palladio complexes are different degradation curves which is inferred that different from each other.

Conclusions

A novel nematic palladio mesogenic moleculeHK-2 and HK-3are synthesized by the treatment of Liquid crystal azobenzene analogues using Bis (benzonitrile) palladium chloride (HK-1) in chloroform at room temperature and isolated complexes are characterized by TLC, FT-IR, LC/MSMS, NMR, and electronic spectroscopy and it reveals the spectra for HK-2 and HK-3 displayed three distinct bands of similar intensity for nematic palladio mesogenic molecules HK-2 and HK-3 and their emission spectra recorded in fluorimetry, further it is observed that these nematic palladio mesogenic molecules HK-2 and HK-3 which exhibited a unique thermal property achieving higher phase transition temperatures and the reduction of mesophase temperature range as compare to that of the liquid crystalline ligands alone and the thermal stability obtained by thermogravimetric analysis (TGA) results shows that palladio mesogenic molecule HK-3is more stable than HK-2.

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Supplementary Information

Supplementary information is available in the website https://nopr.niscpr.res.in/handle/123456789/58776.

Disclosure Statement

No potential conflict of interest was reported by the author.

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