

Electronic Supporting Information (ESI)

Optically biaxial interdigitated smectic A phase : liquid crystalline dimeric bidentate ligands and their metal complexes

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General Information

The solvents (methanol, ethanol, acetonitrile and benzene) used for the reactions were distilled and dried according to standard procedures. The metal salts viz., palladium (II) chloride and copper (II) acetate monohydrate obtained from Aldrich, were used without any further purification. All the ligands¹¹ and the metal-complexes were purified by recrystallization choosing appropriate mixture of solvents; while the intermediates, depending upon the need, were purified by both column chromatographic and recrystallization techniques. Chromatography was performed using either silica gel (60-120, 100-200 and 230-400 mesh) or neutral aluminium oxide. For thin layer chromatography, aluminium sheets pre-coated with silica gel (Merck, Kieselgel60, F₂₅₄) were employed. Infrared spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer; the spectral positions (absorption maxima) are given in wave numbers (cm⁻¹). ¹H NMR spectra were recorded using Bruker AMX-400 (400 MHz) spectrometer. For ¹H NMR spectra, the chemical shifts are reported in ppm relative to SiMe₄ (TMS) as an internal standard and coupling constants are presented in Hz. Elemental analysis were performed using a Eurovector model EA3000 CHNS elemental analyzer. Mass spectra were determined on a JOEL JMS-600H spectrometer in FAB⁺ mode using 3-nitrobenzyl alcohol as a liquid matrix. The initial phase transitions and corresponding temperatures for the complexes were determined by a polarizing optical microscope (POM) (Leitz DMRXP or Leica DMLP) equipped with a Mettler FP82HT hot stage controlled by a Mettler FP90 central processor. Initially, the optical textural observations were performed using untreated clean glass slides; for confirmation of mesophases two differently surface-coated slides, one treated for planar alignment, the other for

homeotropic alignment were used. The phase transition temperatures and associated enthalpies were determined from thermograms recorded at a scanning rate of 5 °C/min on a differential scanning calorimeter (Perkin Elmer DSC-7) calibrated using pure indium as a standard. X-Ray diffraction studies were carried on both aligned and powder samples filled in Lindemann capillaries. These experiments were performed using CuK α radiations ($\lambda = 1.5418 \text{ \AA}$) from a fine focus sealed-tube generator (Enraf Nonius FR590), in conjunction with Image plate setup.

Structural characterization of copper complexes

DCu-7: A brown solid; IR (KBr pellet): ν_{\max} in cm^{-1} 2925, 2858, 2225, 1605, 1436 and 1176; MS (FAB⁺): m/z for C₈₆H₁₀₃N₄O₆Cu (M+1), Calculated: 1350.3, Found: 1351.5. Anal. calc for C₈₆H₁₀₂N₄O₆Cu; C, 76.44; H, 7.61; N, 4.15. Found: C, 76.78; H, 7.31; N, 4.14.

DCu-8: A brown solid; IR (KBr pellet): ν_{\max} in cm^{-1} 2923, 2852, 2225, 1604, 1436 and 1176; Anal. calc for C₈₈H₁₀₆N₄O₆Cu; C, 76.63; H, 7.75; N, 4.06. Found: C, 76.35; H, 8.07; N, 3.95.

DCu-9: A brown solid; IR (KBr pellet): ν_{\max} in cm^{-1} 2923, 2852, 2225, 1604, 1436 and 1176; Anal. calc for C₉₀H₁₁₀N₄O₆Cu; C, 76.81; H, 7.88; N, 3.98. Found: C, 76.78; H, 7.31; N, 4.0.

DCu-10: A brown solid; IR (KBr pellet): ν_{\max} in cm^{-1} 2924, 2852, 2226, 1603, 1436 and 1175; Anal. calc for C₉₂H₁₁₄N₄O₆Cu, C, 76.98; H, 8.0; N, 3.90. Found: C, 76.93; H, 7.36; N, 4.01.

Structural characterization of palladium complexes

DPd-7: A yellow solid; IR (KBr pellet): ν_{\max} in cm^{-1} 2920, 2852, 2224, 1604, 1423 and 1198; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, $J = 8.0 \text{ Hz}$, 4H, Ar), 7.63 (d, $J = 8.3 \text{ Hz}$, 4H, Ar), 7.56 (s, 2H, CH=N), 7.53 (d, $J = 8.5 \text{ Hz}$, 4H, Ar), 7.21 (d, $J = 8.4 \text{ Hz}$, 4H, Ar), 7.18 (d, $J = 8.3 \text{ Hz}$, 4H, Ar), 7.01 (d, $J = 7.9 \text{ Hz}$, 2H, Ar), 6.99 (d, $J = 8.1 \text{ Hz}$, 4H, Ar), 6.12 (dd, $J = 8.7, J = 1.7 \text{ Hz}$, 2H, Ar), 5.5 (d, $J = 1.7 \text{ Hz}$, 2H, Ar), 4.00 (t, $J = 6.5 \text{ Hz}$, 4H, 2 × OCH₂),

3.77(t, $J = 6.5$ Hz, 4H, $2 \times \text{CH}_2$), 2.6 (t, $J = 7.7$ Hz, 4H, $2 \times \text{Ar-CH}_2$), 1.83-1.26 (m, 52H, $26 \times \text{CH}_2$), and 0.87 (t, $J = 6.6$ Hz, 6H, $2 \times \text{CH}_3$); MS (FAB⁺): m/z for $\text{C}_{86}\text{H}_{102}\text{N}_4\text{O}_6\text{Pd}$; Calculated: 1392.6, Found: 1392.8. Anal. calc for $\text{C}_{86}\text{H}_{102}\text{N}_4\text{O}_6\text{Pd}$; C, 74.09; H, 7.37; N, 4.02. Found: C, 74.53; H, 7.1; N, 3.88.

DPd-8: A yellow solid; IR (KBr pellet): ν_{max} in cm^{-1} 2924, 2852, 2224, 1605, 1423 and 1198; ¹H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 8.2$ Hz, 4H, Ar), 7.63 (d, $J = 8.3$ Hz, 4H, Ar), 7.56 (s, 2H, CH=N), 7.53 (d, $J = 8.5$ Hz, 4H, Ar), 7.21 (d, $J = 8.4$ Hz, 4H, Ar), 7.18 (d, $J = 8.3$ Hz, 4H, Ar), 7.01 (d, $J = 7.9$ Hz, 2H, Ar), 6.99 (d, $J = 8.1$ Hz, 4H, Ar), 6.12(dd, $J = 8.7, J = 1.7$ Hz, 2H, Ar), 5.5(d, $J = 1.7$ Hz, 2H, Ar), 4.00(t, $J = 6.5$ Hz, 4H, $2 \times \text{OCH}_2$), 3.8 (t, $J = 6.3$ Hz, 4H, $2 \times \text{CH}_2$), 2.6 (t, $J = 7.7$ Hz, 4H, $2 \times \text{Ar-CH}_2$), 1.83-1.26 (m, 56H, $28 \times \text{CH}_2$), and 0.87 (t, $J = 6.6$ Hz, 6H, $2 \times \text{CH}_3$); MS (FAB⁺): m/z for $\text{C}_{88}\text{H}_{106}\text{N}_4\text{O}_6\text{Pd}$; Calculated: 1420.9, Found: 1421.1. Anal. calc for $\text{C}_{88}\text{H}_{106}\text{N}_4\text{O}_6\text{Pd}$; C, 74.32; H, 7.51; N, 3.94. Found: C, 74.67; H, 7.11; N, 3.89.

DPd-9: A yellow solid; IR (KBr pellet): ν_{max} in cm^{-1} 2924, 2852, 2224, 1605, 1423 and 1198; ¹H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 8.4$ Hz, 4H, Ar), 7.63 (d, $J = 8.0$ Hz, 4H, Ar), 7.56 (s, 2H, CH=N), 7.53 (d, $J = 8.0$ Hz, 4H, Ar), 7.21 (d, $J = 8.0$ Hz, 4H, Ar), 7.18 (d, $J = 8.4$ Hz, 4H, Ar), 7.01 (d, $J = 8.0$ Hz, 2H, Ar), 6.99 (d, $J = 8.0$ Hz, 4H, Ar), 6.12(dd, $J = 8.3, J = 1.7$ Hz, 2H, Ar), 5.5 (d, $J = 1.7$ Hz, 2H, Ar), 4.00(t, $J = 6.5$ Hz, 4H, $2 \times \text{OCH}_2$), 3.8 (t, $J = 6.3$ Hz, 4H, $2 \times \text{CH}_2$), 2.6 (t, $J = 7.7$ Hz, 4H, $2 \times \text{Ar-CH}_2$), 1.83-1.26 (m, 60H, $28 \times \text{CH}_2$), and 0.87 (t, $J = 6.6$ Hz, 6H, $2 \times \text{CH}_3$); Anal. calc for $\text{C}_{90}\text{H}_{110}\text{N}_4\text{O}_6\text{Pd}$; C, 74.53; H, 7.64; N, 3.86. Found: C, 74.22; H, 7.84; N, 3.84.

DPd-10: A yellow solid; IR (KBr pellet): ν_{max} in cm^{-1} 2920, 2851, 2226, 1605, 1423 and 1195; ¹H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 8.4$ Hz, 4H, Ar), 7.63 (d, $J = 8.0$ Hz, 4H, Ar), 7.56 (s, 2H, CH=N), 7.54 (d, $J = 8.4$ Hz, 4H, Ar), 7.21 (d, $J = 8.4$ Hz, 4H, Ar), 7.18 (d, $J = 8.3$ Hz, 4H, Ar), 7.01 (d, $J = 7.9$ Hz, 2H, Ar), 6.99 (d, $J = 8.1$ Hz, 4H, Ar), 6.12(dd, $J = 8.7, J = 1.7$ Hz, 2H, Ar), 5.5 (d, $J = 1.7$ Hz, 2H, Ar), 4.00(t, $J = 6.8$ Hz, 4H, $2 \times \text{OCH}_2$), 3.8 (t, $J = 6.3$ Hz, 4H, $2 \times \text{CH}_2$), 2.6 (t, $J = 7.7$ Hz, 4H, $2 \times \text{Ar-CH}_2$), 1.83-1.26 (m, 64H, $32 \times \text{CH}_2$), and 0.87 (t, $J = 6.6$ Hz, 6H, $2 \times \text{CH}_3$); Anal. calc for $\text{C}_{92}\text{H}_{114}\text{N}_4\text{O}_6\text{Pd}$; C, 74.75; H, 7.77; N, 3.79. Found: C, 74.94; H, 7.14; N, 3.9.

Table S1: Electronic absorption spectral data obtained for the micromolar solutions (in CH₂Cl₂) of dimeric bidentate ligands and their Cu(II) and Pd(II) complexes

Compounds	λ (nm)	ϵ (LMol ⁻¹ cm ⁻¹)	λ (nm)	ϵ (LM ⁻¹ cm ⁻¹)
DL-5	296.2	4705.3	345.5	2777.4
DL-6	296.2	3834.2	345.5	2148.2
DL-7	296.2	1348.2	345.5	811.70
DL-8	296.2	2286.6	345.5	1287.9
DL-9	296.2	4512.1	345.5	2557.2
DL-10	296.2	4208.8	345.5	2215.7
DCu-6	303.4	10941.5	366.6	4683.9
DCu-7	303.4	16098.9	366.6	6585.4
DCu-8	303.4	18712.6	366.6	6286.7
DCu-9	303.4	15244.1	366.6	4824.7
DCu-10	303.4	17139.6	366.6	6818.2
DPd-6	302.4	15999.3	402.6	2960.3
DPd-7	302.4	13780.8	402.6	2853.4
DPd-8	302.4	14042.3	402.6	2890.0
DPd-9	302.4	15366.6	402.6	2899.2
DPd-10	302.4	16052.3	402.6	2881.4

The absorption band occurring in the region of 367-403 nm for the metal complexes can be ascribed to *d-d* transition that supports their square planar geometry: see for example, (a) N.Raman, V.Muthuraj, S.Ravichandran and A.Kulandaisamy, *Pro. Indian Acad. Sci. (Chem.Sci)*, **2003**, *115*, 161. (b) A. H. Al-Kubaisi, *Bull. Korean Chem.Soc.*, 2004, **25**, 37. (c) N. Raman, J. Dhavethu Raja and A. Shakthivel, *J.Chem.*, 2007, **119**,303. (d) M. Tuncel, A. Ozbulbul and S. Serin, *Reac. Funct. Polym.* 2008, **68**,292. (e) H. Furuta, H. Maeda and A. Osuka, *Inorg. Chem. Commun.* 2003, **6**, 162. (f) B. Bilgin-Eran, C. Yorur and S. Uzman, *J. Orgmet. Chem.* 2002,**655**,105.

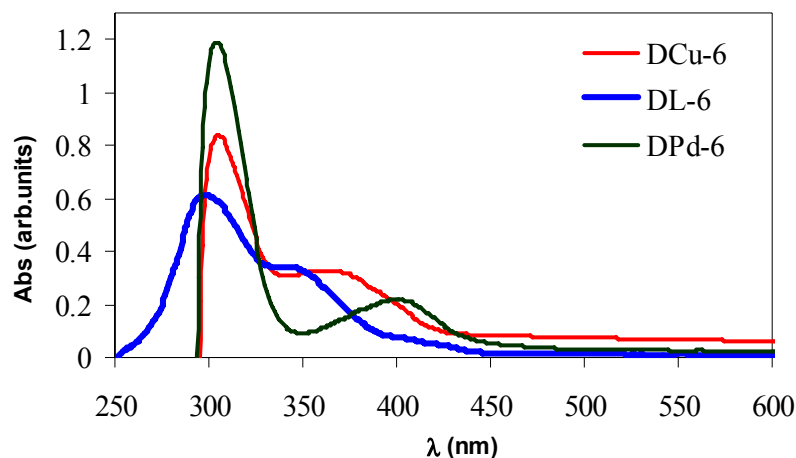


Figure S1: Electronic absorption spectra of ligand **DL-6** and its Cu(II) and Pd(II) complexes in CH₂Cl₂

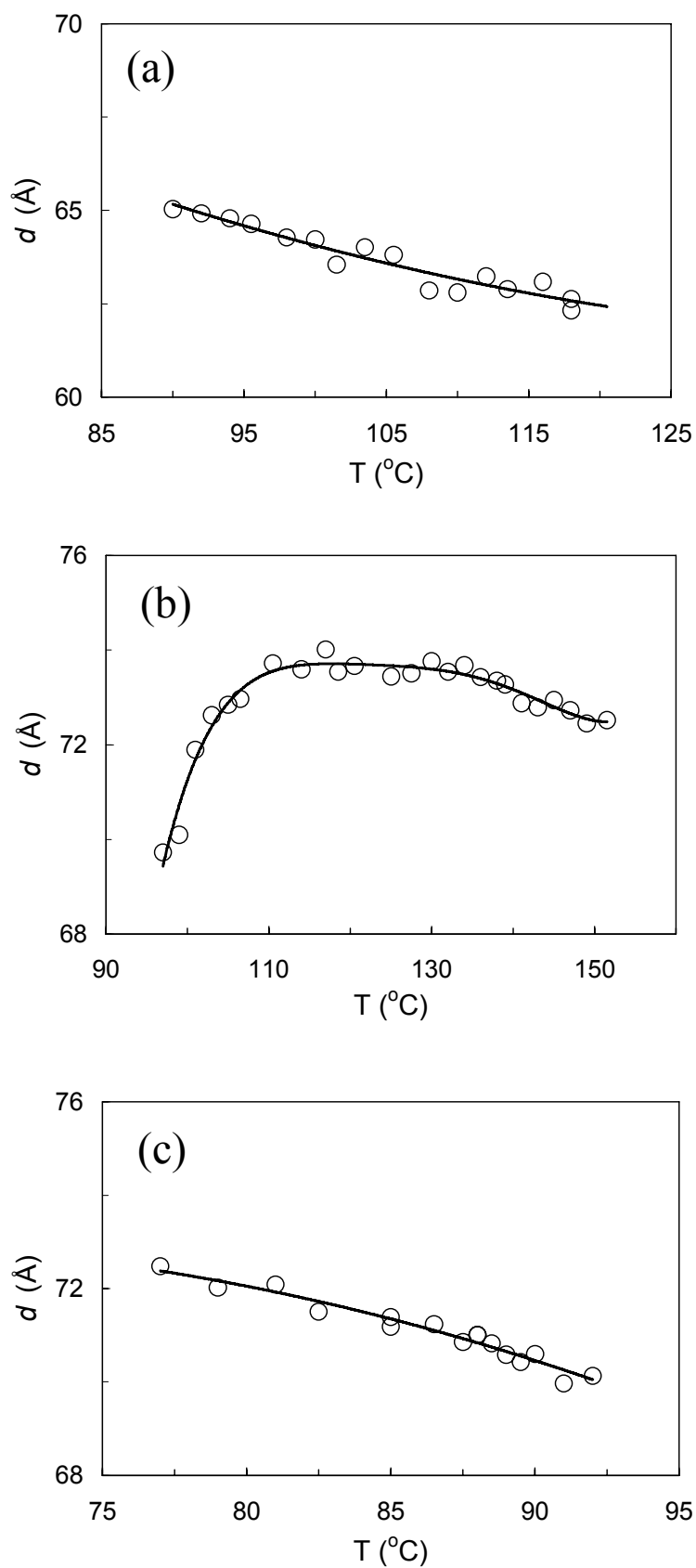


Figure S2: The layer spacing (d) as a function of temperature obtained in the smectic phases on cooling through the I-N phases for dimers (a) **DL-5**, (b) **DL-6** and (c) **DL-7**

Table S2: Estimated molecular lengths ($l/\text{Å}$), layer spacings ($d/\text{Å}$), d/l ratio and structural assignment of the smectic phases of dimers.

Dimer ($l/\text{Å}$)	Temperature /°C	$d/\text{Å}$	d/l	Mesophase
DL-5 (40.1)	118	62.6	1.56	SmA _d
	95.5	64.8	1.62	SmA _{db}
DL-6 (41.3)	151.5	72.5	1.76	SmA _d
	99	70.1	1.68	SmC _a
DL-7 (42.7)	90	70.6	1.65	SmA _d
	82.5	71.5	1.67	SmA _{db}
DL-10 (46.1)	110	23.6	0.5	SmA _c

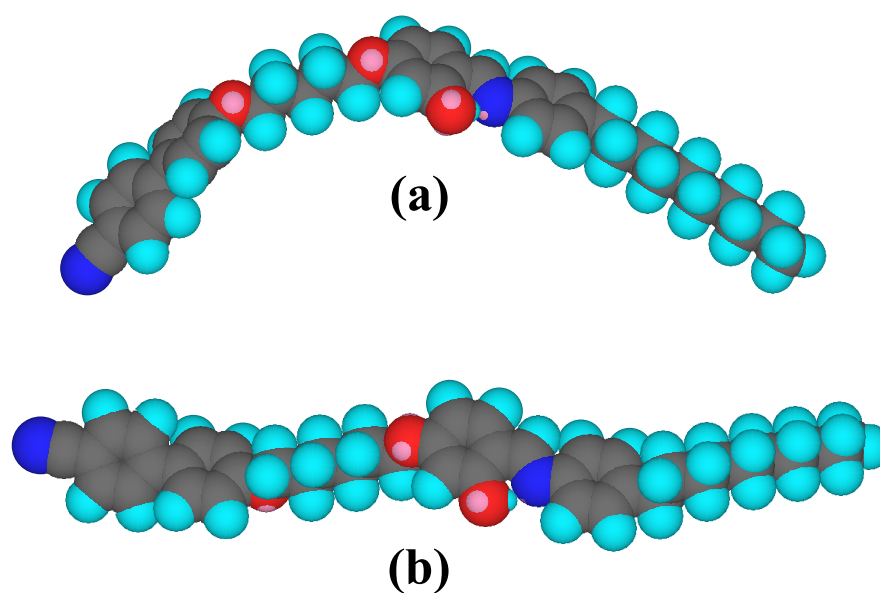


Figure S3: Space filling models of energy minimized molecular structures of dimeric ligands **DL-5** (a) and **DL-6** (b).